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Research Article

Elemental Enrichments Compared to Global Average Anoxic Environments of Oil Shales in the Sorgun-Yeni Çeltek (Yozgat, Türkiye)

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Abstract

In this study, the element enrichment of the Çeltek Formation oil shales located in the Yeni Çeltek coal mine field in the Sorgun district of Yozgat province and the economic mineral deposit potential were investigated. The ICP-MS (ICP mass spectrometry) technique was used for elemental analysis, and the Rock-Eval VI device was used to determine the amount of organic matter in rocks. Total Organic Carbon (% TOC) contents of oil shale samples belonging to 2 different boreholes and one measured stratigraphic section (MSS) made on the surface in the study area vary between 1.37-11.8 wt% (average 4.96% wt%). Major and trace element contents obtained from the samples were compared with the major and trace element values of standard environments known to have anoxic conditions worldwide. According to these results, petroleum products from the Çeltek Formation oil shales and naturally occurring radioactive materials such as U, Th, and K, especially from the remaining liquid rocks and ash, and Mn, Mg, Pb, Zr, Sr, K, Ti, Ca, and Rb. In order to acquire elements such as U and Co, new scientific research in which different disciplines (such as chemistry and metallurgy) will work together needs to be deepened.

Keywords: Trace elements, Oil shale, Total organic carbon (%TOC), Elemental enrichment

1. INTRODUCTION

The study area is located within the boundaries of the Sorgun district of Yozgat province in the northeastern region of Central Anatolia. Sorgun district is surrounded by Akdağmadeni and Saraykent to the east, Sarıkaya to the south, Çekerek to the north and Yozgat-Center to the west.

The study area is located very close to the center of Sorgun and is about 35 km away from Yozgat city center in the northeastern region of Central Anatolia (Figure 1). The area between Çankırı-Çorum-Yozgat was subject to very active tectonism during the Lower Tertiary and was divided by faults and fold axes, forming many sedimentary basins here. The Sorgun Basin, one of these basins, is a long and narrow branch of the Çankırı-Çorum-Yozgat Tertiary Basin that advanced eastward.

The oil shales, which are the main material of the study, are located in the Çeltek Formation. This formation is generally 250-300 m thick and consists of sandstone, coal, oil shale, lenticular sandstone, and mudstone [1]. The Çeltek Formation starts with the sandstones overlying the Yozgat granitoid and continues on the sandstones with coal layers of different thickness in different parts of the basin. Brown and light brown oil shale packages were deposited on this coal, varying from 2 to 50 m throughout the basin. There are 1.6 billion tons of oil shale reserves in Türkiye and the Çeltek Formation has a important potentialwith a probable reserve of 90,000 tons, and their average calorific value is reported to be 541 kcal/kg [1].

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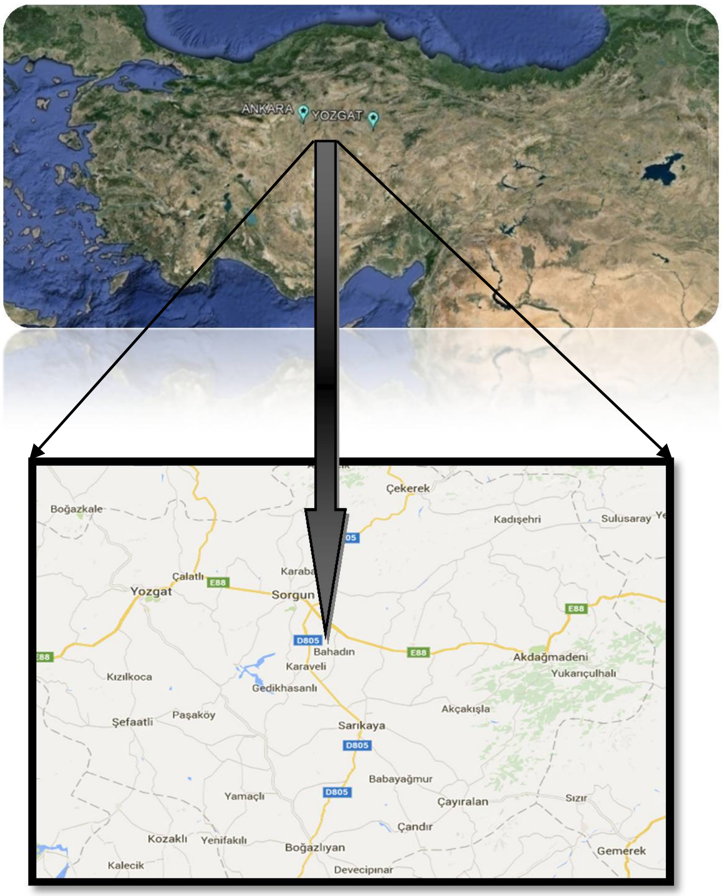

Figure 1. Site plan of the study area

Studies conducted by the USGS claim that world oil shale reserves are 3 trillion barrels, which is more than twice the world's crude oil reserves. The oil equivalent reserves of oil shale in the world are 626 billion barrels in the US, 300 billion barrels in Brazil, 41 billion barrels in Russia, 38 billion barrels in Zaire, 17 billion barrels in Australia, and 16 billion barrels in Canada and Italy. It is estimated that 600-800 billion barrels of the 6 trillion barrels of oil shale calculated in the U.S. can be economically extracted [2].

Oil shale production started in 1916 and reached an annual production of 41 million tons in 1980. In Estonia, it is used to produce electricity, gas, liquefied hydrocarbons, and other chemical products. from 1 ton of oil shale 850 kWh of electric energy and 125 kg of oil are obtained. Oil shale is produced at various scales in Germany, Israel, and Russia, and numerous oil shale projects are in the planning phase in countries such as Australia, Jordan, and Morocco. In the U.S., there are commercial-scale research and implementation projects in Colorado and Utah.

Oil shales are fine-grained rocks of various lithologies that contain refractory organic matter that can be refined into fuel. The soluble portion makes up about 20% of the organic matter, while the remainder is insoluble kerogen (about 5-50%). All oily shales are composed largely of algal biota. They are usually stored in shallow lakes, swamps, or seas. Thank you for your technological progress, oil shales will be one of the most important energy sources in the near future and will gain importance in exploration and research. Oil shales have a great diversity in terms of composition, lithological association, and origin. Today, oil shales are used as the main energy source in many countries. For example, the estimated reserves in China are $2x10^{12}$ tons, which is equivalent to 80 billion tons of shale oil. According to this ratio, China ranks fourth after the USA, Brazil, and Estonia [2]. Oil shale is an important resource that can be used for the production of synthetic oil and gas, as a solid fuel in thermal power plants, as a raw material for cement from shale residues, as a fertilizer and soil stabilizer in agriculture, for the production of adsorption carbon and activated carbon, and for the enrichment of rare elements and metals contained in it.

The main elements contained in oil shale are Al, Ca, Fe, Mg, K, Si, and Na. Trace elements are B, Ba, Cr, Cu, Li, Mn, U, Mo, Ni, Pb, Rb, Sr, Ti, V, Zn, Re, Os, etc.

The main and trace elements can be obtained in the first stage of exploitation of oil shale or with the help of technologies for the enrichment of the remaining ash. For example, in the so-called Rohrbach process, established in Dotternhausen (Germany), electrical energy is obtained by burning oil shale, and valuable trace elements (such as Rb, Sr, Ti, V, Zn, and U) are obtained by enriching the elements contained in the burned ash. The remaining unusable wastes are used to produce cement raw materials [3].

The inorganic constituents of oil shale generally consist of clays (mainly illite and chlorite), carbonate (calcite and dolomite), feldspar, sulfide, sulfate, zeolite, pyrite, evaporite minerals, and quartz. These inorganic components provide important information about the precipitation environment and precipitation conditions. Minerals representing inorganic components in organic material also provide information about climate, living species, the chemical character of solution, and alteration.

In the future, it is inevitable to study the oil shale resources that have the potential to be mineral deposits in our country and in the world, and to evaluate possible resources. In this context, the main and trace elements found in the oil shales of the study area, in the shelf sediments of the Peruvian Coast, in the shelf sediments of the Namibian Coast, in the sediments of the Gulf of Calif, in the Mediterranean Sea Sapropel, in the Black Sea Sapropel, in the anoxic sediments of the Cenoman/Turon (C/T) Demerara Uplift and in the anoxic sediments of the C/T Gubbio, were compared with the major and trace element values. The enrichment of major and trace element concentrations was determined in the studied samples compared to the average shale.

2. GEOLOGICAL SETTING

The oldest units observed in the study area and its surroundings is the Central Anatolian granitoid. The Çeltek Formation of the Lower Eocene age unconformably overlies the Central Anatolian granitoid. This unit is followed unconformably by the Boğazköy Formation of the Lower to Middle Eocene age. This formation unconformably overlies the Çekerek Formation of the Middle-Upper Eocene age. Overlying the Çekerek Formation are the tectonically displaced Darmik Formation of the İzmir-Ankara-Erzincan Zone, as well as the rocks of the Artova ophiolite complex and the Middle Miocene to Quaternary sediments, which unconformably overlie this entire sequence. The unit consisting of ophiolitic rocks in the study area, the so-called İzmir-Ankara-Erzincan-Sutten belt, overlies the Boğazköy Formation as a result of Late Lutetic horizontal movements. All these units are covered by Neogene sediments [4,5].

The unit in which the oil shales are deposited is the Çeltek Formation. This formation starts with sandstones overlying granitoid. The sandstones are white-light gray in the underground mining areas. There is a charcoal layer of varying thickness on the sandstones. Above the coal layer, there are brown and light brown oil shales with a thickness of 2-3 m and sandstone layers of 5-10 cm in between. The thickness of the oil shale reaches up to 50 m in some boreholes. Lenticular sandstone and mudstone interbed overlie the oil-bearing shale layers. This is followed by a 50 cm thick mudstone layer, 1-1.5 m thick, light yellow colored, weakly consolidated, sandy-gravelly units consisting mainly of coarse sand and occasionally fine gravelly material, and 30 cm thick mudstone layers marked with cha

3. MATERIAL AND METHOD

The research material consists of samples representing the Çeltek Formation. For the study, the samples were collected from three different points, one surface (YC MSS) and two boreholes (SJ and C). The surface samples were collected using a systematic MSS study. Samples from the boreholes (SJ and C) were collected approximately 10 cm from each meter (Figure 2). A total of 29 oil shale samples were evaluated in this study. In addition, 3 samples from Estonia, Utah, and Jordan, which can be considered as references in different parts of the world, were included in our study. the percent TOC content of rocks, S1-S2-S3 hydrocarbons, Tmax, PI, HI, and OI were determined by pyrolysis analysis, where data such as [6] can be obtained. Pyrolysis analysis was performed in the laboratories of the TPAO organic geochemistry research group using the IFP 160000 (Institut Français du Pétrole) standard on a Rock-Eval VI instrument. The TOC content in the rock is a minimum of 1.37 wt%, a maximum of 11.8 wt%, and an average of 4.96 wt%. To better determine elemental enrichments in the basin, only oil shale samples were analyzed. Inorganic geochemical analyzes of samples pulverized in agate mortar were performed at ACME Analytical Laboratories Ltd (Canada) using the techniques ICP-ES (ICP emission spectrometry) and ICP-MS (ICP mass spectrometry). The element abundances obtained were interpreted by comparison based on rocks, and their geochemical behavior was studied by calculating the correlation coefficients. The enrichment values of the elements belonging to our study area were compared with the elements in other reducing environments known worldwide. Thin sections were prepared from 12 samples for petrographic and mineralogical studies and examined under a Leica-DM-EP microscope. The thin sections were prepared using Araldite from samples in rock laboratories on a standard 28 x 48 x 1 mm glass slide (lam) in the mineralogy and petrography laboratories of the MTA-MAT department. It was ground in the laboratories of Yozgat Bozok University

Geological Engineering laboratories were determined and interpreted by XRD analyses in the laboratories of the Department of Mineralogy and Petrography of the MTA, MAT. XRD analyses were performed using a Philips Panalytical XRD instrument with a Cu X-Ray tube.

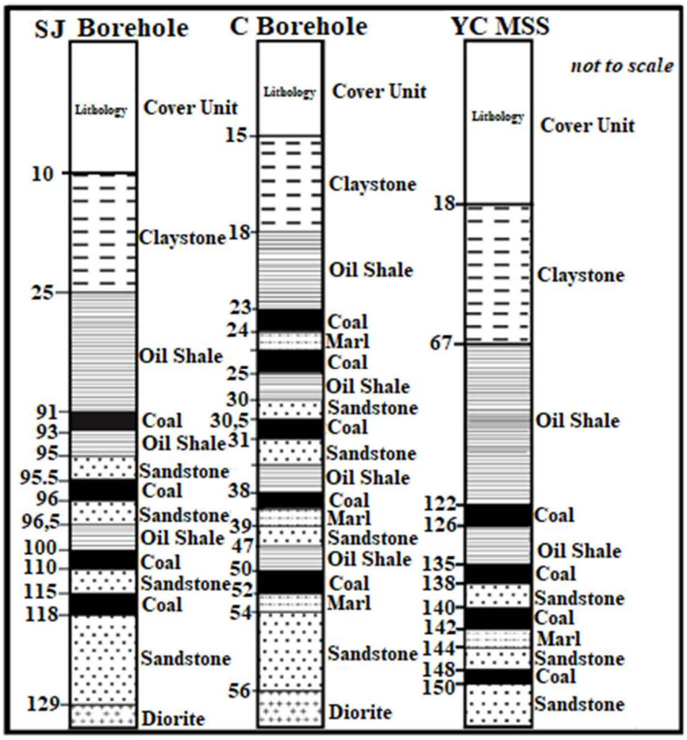

Figure 2. Type section of SJ-C borehole and YC MSS (not to scale)

4. RESULTS AND DISCUSSION

4.1. Mineralogical Analysis

In this study,mineralogical and textural analyses, mineral characterization, the quantitative abundance of minerals, mineral chemistry, and mineral paragenesis are analyzed for determination.Thin sections were selected from the samples at different depths where the depth-dependent changes in the samples and prepared and analyzed to determine the mineralogical and textural composition of oil shale and other rock samples rich in organic matter, and XRD analyses of powder samples were performed.These analyses were used to determine the mineral constituents and structure-texture relationships of the rocks. The mineral constituents of the rocks were determined by XRD analysis.

Oil shale is found in sedimentary rocks and generally contains clay minerals (kaolinite, smectite, illite, chlorite), carbonate minerals (calcite, dolomite), minerals such as quartz, feldspar, pyrite, and organic matter as mineral components. The strata of the Çeltek Formation generally consist of an alternation of sandstone, coal, oil shale, lenticular sandstone, and mudstone. The drill samples collected in the study area completely cut the oil shale layer. Fine-grained quartz and feldspar minerals are observed in a homogeneous distribution. Opaque organic material in the form of fine lines is cutinite (Figure 3). Small- to medium-grained crystalline quartz minerals; feldspar minerals as small-to-medium-grained homogeneously distributed crystals; and opaque minerals as small-grained crystals are observed. Its binder is carbonate. The rock's name was determined to be sandstone (Figure 4). Minerals such as quartz, calcite, dolomite, biotite, and feldspar were detected in these samples, which are rich in organic material.

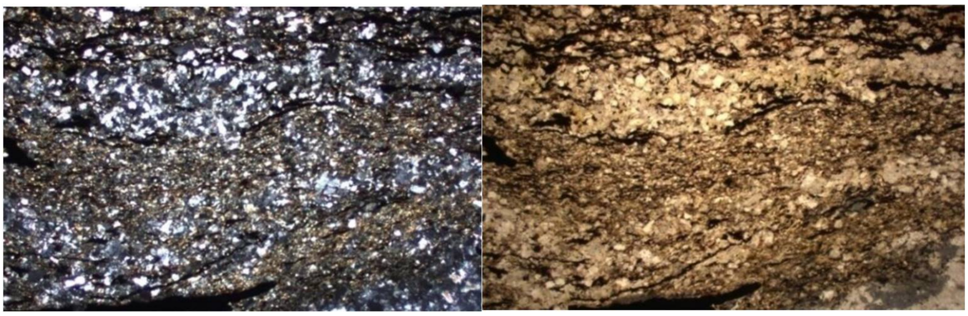

Figure 3. Small-grained quartz, feldspar minerals and, organic material in oil shale samples

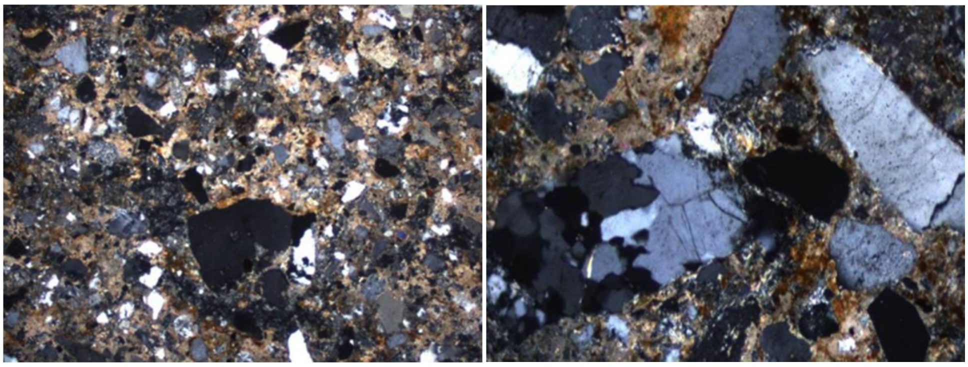

Figure 4. Feldspar and quartz crystal in sandstone

Quartz, feldspar, dolomite, calcite, pyrite, gypsum, analcime, and clay minerals were determined in the samples with XRD analysis. In the borehole samples, the predominant mineral is quartz. Feldspar and clay minerals are other common minerals. In addition, calcite, dolomite, pyrite, and gypsum are also present in varying proportions (Tables 1 and 2).

Table 1. Minerals detected by XRD in the C boreholes samples

Sample	Quartz	Feldspar	Calcite	Dolomite	Pyrite	Kaolinite	Chloride	Mica/Illite
Ç.1	+	+	-	-	+	+	+	+
Ç.2	+	+	-	-	+	-	+	+
Ç.3	+	+	-	-	+	+	-	+
Ç.4	+	-	+	-	+	-	+	+
Ç.5	+	-	+	-	+	-	+	+
Ç.6	+	-	+	-	+	+	-	-
Ç.7	+	-	-	-	+	+	-	+
Ç.8	+	+	+	-	+	+	-	+
Ç.9	+	+	+	-	+	+	-	+
Ç.10	+	+	-	-	+	+	-	-
Ç.11	+	-	-	-	+	-	+	+
Ç.12	+	-	-	-	+	+	-	+
Ç.13	+	+	-	-	+	+	-	-
Ç.14	+	+	+	+	+	+	+	+
Ç.15	+	+	-	+	-	+	-	+
Ç.16	+	+	-	+	-	+	-	+
Ç.17	+	+	+	+	+	+	+	+
Ç.18	+	+	-	-	-	+	-	+
Ç.19	+	+	+	-	+	-	-	+
Ç.20	+	+	-	-	+	+	-	+
Ç.21	+	-	+	-	+	+	-	+
Ç.22	+	-	-	-	+	+	-	+
Ç.23	+	-	-	-	-	+	-	+
Ç.24	+	-	-	-	+	+	-	+
Ç.25	+	+	-	-	+	+	-	+
Ç.26	+	-	-	-	+	+	-	+
Ç.27	+	-	-	-	+	+	-	+
Ç.28	+	-	-	-	-	+	-	-
Ç.29	+	-	-	-	-	+	-	-
Ç.30	+	-	-	-	+	+	-	-
Ç.31	+	-	+	+	+	+	-	-
Ç.32	+	+	-	-	+	+	-	-
Ç.33 a	+	-	-	-	+	+	-	-
Ç.33 b	+	-	-	-	-	+	-	-
Ç.34	+	+	-	-	-	+	-	-
Ç.35	+	-	-	-	-		-	+

Table 2. Minerals detected by XRD in the SJ boreholes samples

Sample	Quartz	Feldspar	Calcite	Pyrite	Gypsum	Kaolinite	Chloride	Mica/Illite	Smectite
SJ.1	+	+	-	-	-	-	+	+	-
SJ.2	+	+	+	-	-	+	+	+	+
SJ.3	+	-	+	-	-	-	+	+	-
SJ.4	+	+	+	-	-	+	-	+	-
SJ.5	+	+	+	-	-	+	-	+	-
SJ.6	+	+	+	-	-	-	+	+	-
SJ.7	+	+	+	-	-	-	+	+	-
SJ.8	+	+	+	-	-	-	+	+	-
SJ.9	+	+	+	-	-	+	+	+	-
SJ.10	+	+	-	-	-	+	+	+	-
SJ.11	+	+	+	-	-	-	+	+	-
SJ.12	+	+	-	+	+	+	+	+	-
SJ.13	+	+	-	-	-	+	+	+	-
SJ.14	+	+	-	-	-	+	+	+	+
SJ.15	+	+	-	+	-	+	+	+	-
SJ.16	+	+	-	-	-	+	+	+	+
SJ.17	+	+	-	-	-	-	+	+	-
SJ.18	+	+	-	-	-	+	+	+	+
SJ.19	+	+	-	-	-	+	+	+	-
SJ.20	+	+	-	-	-	+	+	+	-
SJ.21	+	+	-	-	-	+	+	+	-
SJ.22	+	+	-	-	-	+	+	+	-
SJ.23	+	+	+	-	-	+	+	+	+
SJ.24	+	+	+	+	-	-	+	+	-
SJ.25	+	+	+	-	-	+	+	+	+

4.2. Total Organic Matter (TOC)

Total organic carbon (TOC) is the sum of the carbon content of the kerogen and hydrocarbons derived from the kerogen but not removed from the rock [7]. The potential of source rock and TOC values of different researchers are shown in Table 3. TOC values of oil shale of Çeltek formation; TOC_{min}: 1.37 %, TOC_{max}: 11.8 %, TOC_{mean}: 4.96 %. According to the values given in Table 1, the study area is in the range of "very good - excellent" in terms of source rock quality. However, these values in Table 1 are for petroleum source rocks. TOC values % for oil shale, < 4 % uneconomical, 4-10 % moderately economical, and > 10% High/very economical have been determined. Based on these results, the samples in the study area can be considered moderately economical.

Table 3. TOC values and source rock quality

Jarvie (1991)[8]		**Tissot ve Welte (1984)[9]**		**Peters ve Cassa (1994) [10]**	
TOC(%)	Source Rock Quality	TOC(%)	Source Rock Quality	TOC(%)	Source Rock Quality
0-0.5	Insufficient	0.1-0.5	Weak	0-0.5	Weak
0.5-1	Middle	0.5-1	Middle	0.5-1	Middle
>1	Sufficient	1-2	Good	1-2	Good
		2-10	Rich	2-4	Very Good
				>4	Excellent

4.3. Trace Element Contents of Oil Shales

Geochemistry is often very important for interpretations related to elements, constituents, and isotopes, and especially for quantitative analyses. The geochemical distribution of major (> 1%), minor (0.1-1%), and trace elements (0.1%) reflects the character of the depositional environment of the host sediments. Using the abundance values of a single element to interpret the character of a geologic environment can produce misleading results, but element ratios can be used to interpret the environment [11]. All adsorbed elements, from ambient water to organic and inorganic materials, can be used to determine the reservoir environment. These indicator elements may be retained in primary minerals or in organic matter formed in the surrounding waters, or they may be retained by the growth of authigenic minerals during sedimentation or immediately after storage [12]. In addition to trace element abundances, all rock components, isotope ratios, exchangeable cations, and geochemical processes are used to determine the storage environment.

All samples studied in this project consist primarily of carbon-rich shales, limestones, and marls. The shale samples were specifically analyzed for geochemical studies. The ICP method was used to determine the presence and abundance of major, minor, and rare earth elements in the oil shale samples of the Çeltek Formation of the Sorgun Basin, and charts and graphs were prepared (Tables 4 and 5; Figures 5 and 6).

After analyzing the collected samples, the average values of element abundances were compared with those of the Estonian, Utah, and Jordanian shales, which we used as reference values in Tables 4 and 5.

Table 4. Average values of the main elements of the oil shale samples from the Çeltek formation

	SiO_2	**Al_2O_3**	**Fe_2O_3**	**MgO**	**CaO**	**Na_2O**	**K_2O**	**TiO_2**	**P_2O_5**	**MnO**	**Cr_2O_3**
EST	10.11	2.23	0.99	0.65	13.44	0.05	1.21	0.14	0.09	0.01	0.004
UTH	26.83	5.57	3.48	6.23	24.52	1.21	2.46	0.18	0.05	0.03	0.004
URD	19.23	3.51	1.15	0.83	24.53	0.16	0.69	0.17	3.19	0.01	0.068
C avr (n=10)	42.061	20.424	4.188	0.461	1.132	0.173	2.022	0.507	0.06	0.0685	0.00316
YC avr (n=9)	46.38	22.22778	6.253333	0.931111	0.657778	0.192222	2.42	0.486667	0.1	0.118778	0.0051
SJ avr (n=10)	59.942	13.719	4.635	1.281	4.733	1.139	3.912	0.522	0.1	0.0629	0.00539
Basin Average	49.461	18.79026	5.025444	0.891037	2.174259	0.501407	2.784667	0.505222	0.086667	0.083393	0.00455

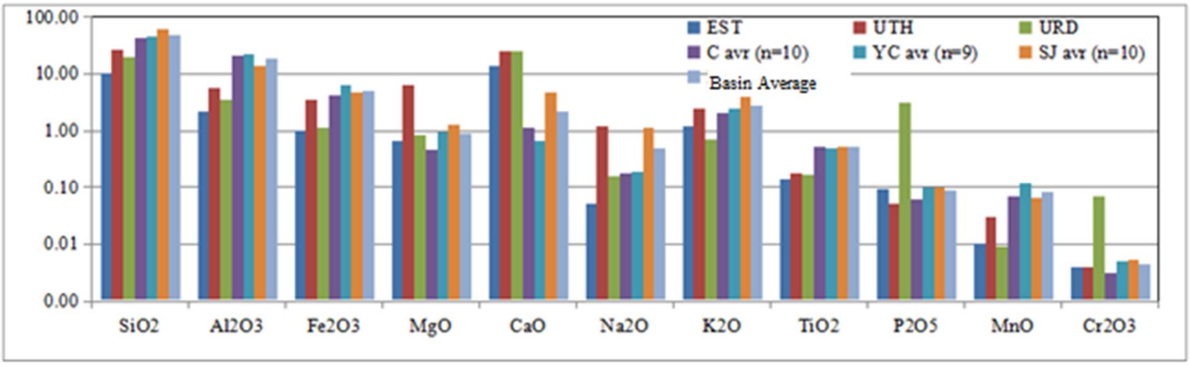

Figure 5. Ratios of major elements of oil shale samples from Çeltek formation of Sorgun basin [5]

Table 5. Average values of trace elements of oil shale samples from Çeltek formation of Sorgun basin

	Ba	Sc	Co	Cs	Ga	Hf	Nb	Rb	Sn	Sr	Ta	Th	U	V	W	Zr	Mo	Cu	Pb	Zn	Ni	As	Cd	Sb	Bi
EST	77.0	2.0	3.2	0.8	1.5	0.9	2.6	22.0	0.9	239.6	0.2	2.5	1.7	20.0	18.7	33.8	1.6	3.5	15.4	5.0	9.9	4.1	0.1	0.1	0.1
UTH	588.0	4.0	17.3	3.3	5.2	1.1	4.3	71.8	0.9	1235.0	0.3	5.2	5.0	54.0	52.9	43.7	12.0	14.6	14.8	33.0	12.8	62.5	0.4	0.8	0.2
URD	53.0	5.0	4.9	0.7	2.9	0.9	3.1	14.2	0.9	751.5	0.2	2.0	31.1	297.0	9.3	38.5	103.1	94.9	6.6	924.0	230.3	6.8	150.3	1.7	0.1
C avr (n=10)	724.1	7.1	10.6	22.5	25.1	5.0	18.2	142.9	4.5	228.8	1.0	63.0	45.6	74.1	34.5	187.0	3.3	18.7	104.1	100.5	7.9	28.6	0.3	0.8	2.7
YC avr (n=9)	370.4	12.0	17.4	20.8	26.9	3.8	13.7	153.3	4.5	185.9	0.8	49.4	13.4	112.6	27.8	132.9	4.0	27.8	72.0	166.0	12.4	34.5	0.4	0.5	2.4
SJ avr (n=10)	732.8	9.3	15.7	37.1	14.8	5.3	13.9	186.1	3.2	409.7	0.9	29.3	81.5	82.5	75.4	214.2	4.5	17.6	41.6	72.1	12.6	39.5	0.2	0.7	0.8
Basin Average	609.1	9.5	14.5	26.8	22.2	4.7	15.3	160.8	4.1	274.8	0.9	47.2	46.9	89.7	45.9	178.0	3.9	21.4	72.6	112.9	11.0	34.2	0.3	0.7	2.0

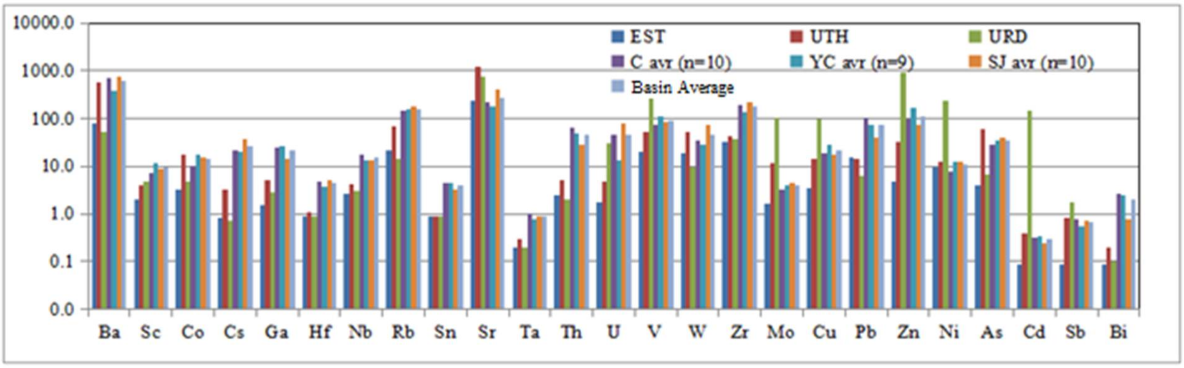

Figure 6. Trace element ratios of oil shale samples from the Çeltek formation of the Sorgun basin [5]

4.4. Element Enrichments

In this study, the element enrichment of the oil shale samples from the Çeltek Formation of the Sorgun Basin was calculated based on various average values in Table 4 for each sample point, which is shown in Tables 6-16 and in Figures 7-14. Element enrichment coefficients were calculated using the element enrichment formula [EFelement X = (X/Al)sample / (X/Al)standard] used by Brumsack [13]. These calculations were also used to determine the depth-dependent enrichment coefficients of all evaluated samples (Tables 6-16). If the value resulting from these calculations is greater than 1, it was interpreted that the analyzed samples were enriched according to the standard values; if it is less than 1, shows that you are consumed.

The average carbonate and shale values of the reference data used were obtained from Turekian and Wedepohl [14], the average elemental values of the Peruvian coast were obtained from Boening et al. [15], the average element values of Namibian Muds were determined by Borchers et al. [16], the average elemental values of the Mediterranean Sea sapropel were obtained from Warning and Brumsack [17], the average elemental values of the Black Sea sapropel were obtained from Jørgensen et al. [18], the average elemental values of C/T Demerara Rise and C/T Gubbio were taken from the studies of Brumsack [13].

The geochemical behavior of trace elements in sediments rich in topical organic carbons, upwelling areas, and anoxic basins has been investigated in numerous studies [19]. Similar studies have been performed on aged oil shales [20,21]. The accumulation of redox-sensitive elements reflects the storage environments of TOC-rich sedimentary rocks and, therefore, is used to indicate the conditions required for their formation [20–22]. Organic carbon-rich rocks such as the Seroman-Turon (Cenoman-Turon boundary event - CTBE) are significantly enriched in sulfide formation and/or redox-sensitive trace elements [17, 21]. In recent TOC-rich sediments in the Black Sea [19,23] and in Norwegian black shale, significant enrichment of some trace elements (except Co and Mo) has been observed. Trace elements such as V, Ag, Bi, Cd, Mo, Re, Sb, Tl, U, Co, Cu, Cr, and Ni have accumulated in the Volgian and Early Berriasian black shale. These elements are strongly retained in the sediments under reducing conditions [19,22,24–26]. They either precipitate as free sulfides and bind to organic material or co-precipitate with Fe sulfides [27].

Table 6. Average reference values

Element/Al	Average Carbonate[13]	Average Shale[13]	Average Peru Marin[14]	Namibian Mud Lenses[15]	Mediterranean Sapropels[16]	Black Sea Sapropels[17]	C/T Demerara Rise[18]	C/T Gubbio [18]
Mn/Al (%)	2619.000	96.000	52.000	28.000	202.000	129.000	42.000	23.000
Mg/Al (%)	11.191	0.188	0.280	0.380	0.390	0.300	0.240	0.230
Fe/Al (%)	0.915	0.590	0.450	0.800	1.220	0.650	0.620	1.330
Si/Al (%)	5.714	0.913	4.330	30.200	2.650	3.080	6.130	16.400
K/Al (%)	0.643	0.333	0.280	0.390	0.250	0.300	0.260	0.370
Ti/Al (%)	0.100	0.053	0.052	0.080	0.061	0.048	0.053	0.044
Ca/Al (%)	71.976	0.276	1.500	2.000	4.070	5.150	8.570	0.220
Na/Al (%)	0.095	0.120	0.980	0.910	0.450	0.980	0.410	0.050
Cr/Al (%)	26.191	11.250	24.400	72.000	28.300	12.200	57.000	33.900
Pb/Al ppm	21.429	2.500	3.500	3.700	2.900	5.300	3.000	16.700
Zr/Al (ppm)	45.238	20.000	21.000	25.200	24.000	18.000	15.000	19.000
P/Al (ppm)	0.095	0.009	0.096	0.170	0.016	0.018	0.070	0.046
Sr/Al (ppm)	1452.381	37.500	86.000	181.000	200.000	271.000	318.000	122.000
Rb/Al (ppm)	7.143	17.500	12.300	22.000	12.100	15.600	11.200	16.700
U/Al (ppm)	5.238	0.463	2.300	28.600	4.100	3.200	4.870	2.900
Ba/Al (ppm)	23.810	72.500	69.000	298.000	341.000	174.000	155.000	3638.000
Cu/Al (ppm)	9.524	5.625	11.600	32.000	33.100	17.600	31.900	63.000
Ni/Al (ppm)	47.619	8.500	20.200	41.000	54.600	16.700	60.000	52.400
As/Al (ppm)	2.381	1.625	4.300	11.000	15.400	4.150	8.600	18.000
V/Al (ppm)	47.619	16.250	38.000	126.000	139.000	29.000	491.000	271.000
Zn/Al (ppm)	47.619	11.875	24.000	29.000	25.000	19.000	246.000	249.000
Sb/Al (ppm)	0.476	0.188	0.500		2.670	0.570	4.380	1.560
Co/Al (ppm)	0.231	2.375	1.200	2.900	17.400	6.200	2.810	5.900
Mo/Al (ppm)	0.714	1.375	10.600	37.000	27.900	14.700	37.700	12.800
Cd/Al (ppm)	0.083	0.075	8.500	26.000	2.700	0.260	5.810	2.140

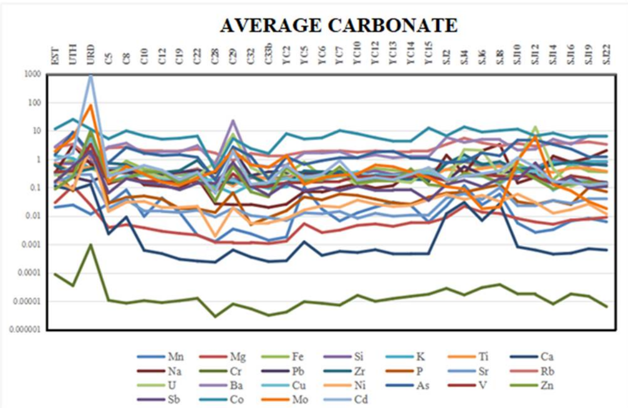

Figure 7. Elemental enrichments compared to average carbonate [13]

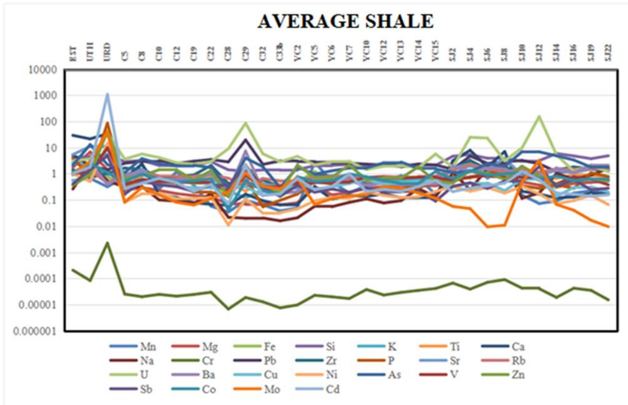

Figure 8. Element enrichments compared to average shale [13]

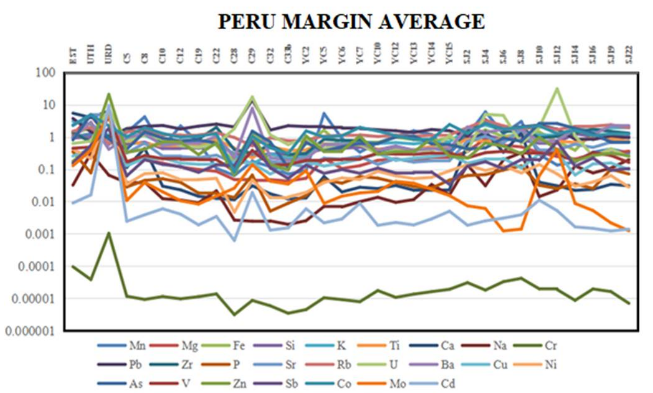

Figure 9. Element enrichments compared to the Peru margin average [14]

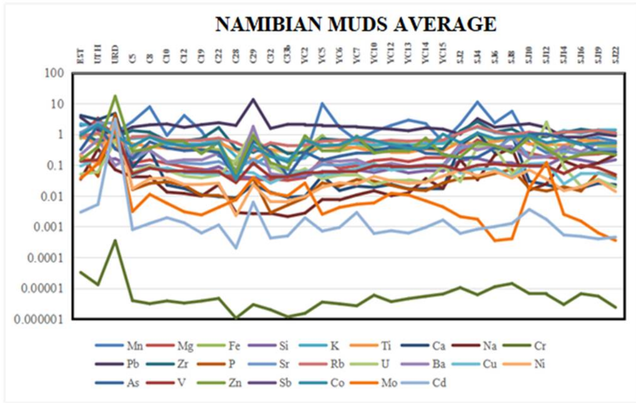

Figure10. Element enrichments compared to the average of Namibian Muds [15]

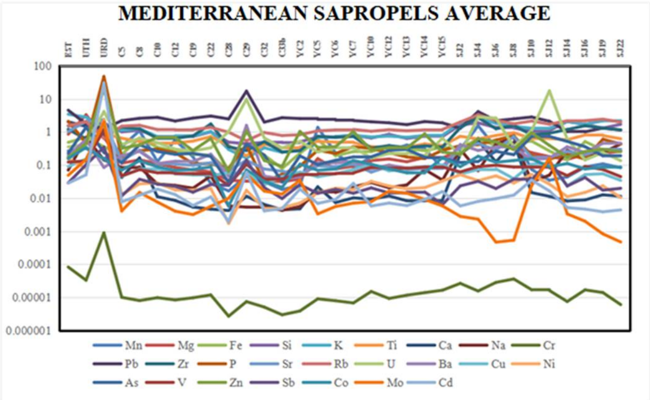

Figure 11. Element enrichments compared to the average Mediterranean Sapropels [16]

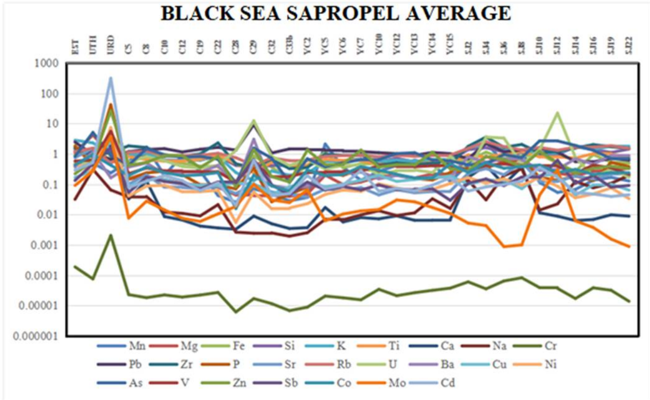

Figure 12. Element enrichments compared to the average Black Sea Sapropel [17]

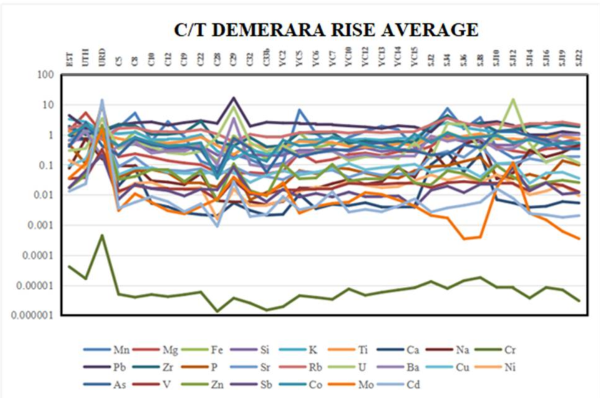

Figure 13. Element enrichments compared to the C/T Demerara Rise average [18]

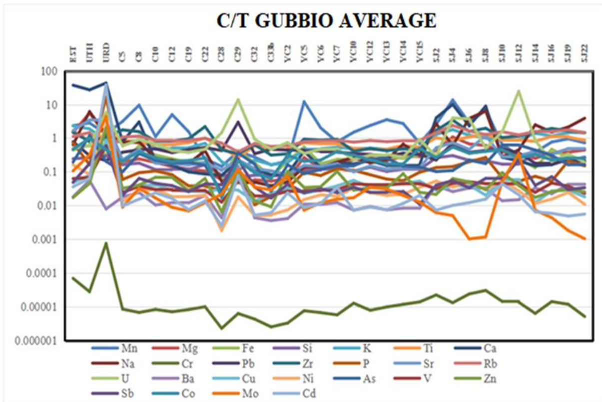

Figure 14. Element enrichment compared to the C/T Gubbio average [18]

Table 7. Element enrichments by carbonate average

Average Carbonate [13]	Mn	Mg	Fe	Si	K	Ti	Ca	Na	Pb	Zr	P	Sr	Rb	U	Ba	Cu	Ni	As	V	Zn	Sb	Co	Mo	Cd
EST	0.020	0.030	0.641	0.701	1.324	0.711	0.113	0.330	0.609	0.633	0.350	0.140	2.610	0.275	2.740	0.311	0.176	1.459	0.356	0.089	0.160	11.737	1.898	0.915
UTH	0.025	0.114	0.903	0.745	1.078	0.366	0.083	3.199	0.234	0.328	0.078	0.288	3.410	0.324	8.377	0.520	0.091	8.904	0.385	0.235	0.570	25.405	5.699	1.629
URD	0.012	0.024	0.473	0.847	0.480	0.549	0.131	0.671	0.166	0.458	7.872	0.279	1.070	3.196	1.198	5.364	2.603	1.537	3.357	10.445	1.922	11.419	77.698	971.282
C5	0.027	0.004	0.274	0.463	0.437	0.390	0.002	0.394	0.295	0.733	0.028	0.019	2.507	0.321	2.709	0.156	0.015	0.754	0.137	0.167	0.065	5.227	0.159	0.248
C8	0.083	0.005	0.860	0.518	0.485	0.315	0.009	0.409	0.347	0.649	0.045	0.038	2.671	0.501	3.689	0.260	0.031	2.606	0.210	0.210	0.207	10.020	0.575	0.394
C10	0.010	0.004	0.454	0.331	0.277	0.278	0.001	0.126	0.371	0.338	0.051	0.015	1.986	0.367	1.570	0.270	0.033	1.655	0.169	0.356	0.148	6.631	0.296	0.605
C12	0.043	0.003	0.352	0.343	0.293	0.278	0.000	0.114	0.287	0.339	0.039	0.015	1.940	0.234	1.846	0.187	0.020	1.352	0.160	0.352	0.126	5.091	0.156	0.412
C19	0.014	0.002	0.280	0.335	0.295	0.321	0.000	0.094	0.352	0.398	0.018	0.013	1.977	0.208	1.814	0.173	0.020	1.445	0.158	0.143	0.084	5.506	0.123	0.192
C22	0.002	0.002	0.264	0.462	0.401	0.437	0.000	0.220	0.407	0.919	0.018	0.016	2.299	0.258	3.032	0.165	0.022	1.169	0.157	0.331	0.143	6.528	0.218	0.350
C28	0.001	0.001	0.088	0.225	0.114	0.234	0.000	0.027	0.331	0.187	0.013	0.009	1.648	0.795	0.652	0.203	0.002	0.189	0.071	0.033	0.135	0.429	0.384	0.063
C29	0.003	0.001	0.612	0.202	0.062	0.116	0.001	0.025	2.297	0.144	0.066	0.019	0.908	7.574	22.361	0.188	0.020	2.724	0.304	0.554	0.777	5.365	2.050	1.932
C32	0.002	0.001	0.263	0.224	0.128	0.257	0.000	0.026	0.266	0.266	0.005	0.010	1.614	0.512	0.656	0.087	0.006	1.270	0.109	0.072	0.115	2.381	0.631	0.132
C33b	0.001	0.001	0.105	0.219	0.093	0.201	0.000	0.020	0.362	0.131	0.009	0.009	1.311	0.254	0.542	0.154	0.006	0.200	0.111	0.047	0.054	1.591	0.515	0.155
YC2	0.002	0.001	0.298	0.230	0.107	0.211	0.000	0.026	0.341	0.143	0.015	0.007	1.388	0.406	0.623	0.212	0.008	1.211	0.150	0.540	0.141	7.947	1.338	0.604
YC5	0.105	0.005	0.790	0.325	0.267	0.316	0.001	0.072	0.323	0.391	0.047	0.013	1.808	0.193	1.668	0.153	0.016	0.661	0.157	0.177	0.078	5.170	0.130	0.222
YC6	0.018	0.003	0.252	0.335	0.278	0.297	0.000	0.070	0.306	0.361	0.037	0.012	1.938	0.257	1.641	0.188	0.023	0.890	0.162	0.188	0.102	5.662	0.216	0.293
YC7	0.007	0.003	0.338	0.364	0.306	0.290	0.001	0.101	0.296	0.383	0.060	0.015	2.000	0.266	1.850	0.251	0.020	1.128	0.168	0.533	0.078	10.219	0.273	0.893
YC10	0.013	0.005	0.333	0.302	0.273	0.218	0.001	0.139	0.273	0.171	0.053	0.008	1.765	0.127	1.107	0.367	0.037	1.136	0.248	0.148	0.114	7.898	0.303	0.186
YC12	0.021	0.005	0.476	0.390	0.290	0.205	0.001	0.096	0.253	0.204	0.039	0.012	1.969	0.173	1.419	0.230	0.026	1.794	0.234	0.176	0.080	5.725	0.626	0.228
YC13	0.031	0.004	0.407	0.293	0.265	0.205	0.000	0.118	0.223	0.176	0.029	0.010	1.824	0.181	1.127	0.267	0.022	1.914	0.231	0.171	0.084	4.345	0.546	0.191
YC14	0.024	0.006	0.362	0.343	0.305	0.264	0.000	0.343	0.277	0.200	0.026	0.011	1.940	0.150	1.265	0.300	0.024	1.104	0.250	0.456	0.086	4.381	0.354	0.294
YC15	0.006	0.006	0.452	0.335	0.306	0.233	0.000	0.165	0.253	0.185	0.047	0.011	2.001	0.501	1.247	0.348	0.038	1.037	0.252	0.128	0.036	12.595	0.225	0.508
SJ2	0.023	0.009	0.421	0.748	0.737	0.448	0.012	1.394	0.173	0.709	0.064	0.043	3.353	0.157	5.898	0.186	0.058	0.764	0.180	0.111	0.131	6.665	0.109	0.187
SJ4	0.118	0.022	0.817	0.865	1.019	0.371	0.030	0.316	0.552	1.432	0.068	0.061	5.523	2.194	3.914	0.251	0.039	0.824	0.260	0.327	0.179	13.756	0.090	0.256
SJ6	0.025	0.014	0.506	0.627	0.698	0.473	0.007	1.995	0.293	0.657	0.095	0.039	3.790	2.039	5.013	0.263	0.054	1.668	0.285	0.261	0.109	9.070	0.018	0.311
SJ8	0.060	0.012	0.605	0.604	0.573	0.572	0.027	3.332	0.333	0.819	0.128	0.099	2.961	0.276	4.793	0.133	0.032	1.319	0.252	0.152	0.207	10.251	0.021	0.395
SJ10	0.006	0.008	0.702	0.482	0.498	0.385	0.001	0.146	0.379	0.433	0.032	0.023	3.590	0.849	2.099	0.365	0.059	4.708	0.250	0.488	0.196	11.476	0.916	1.122
SJ12	0.003	0.006	0.353	0.507	0.499	0.384	0.001	0.232	0.282	0.481	0.025	0.023	2.888	13.577	2.259	0.390	0.030	4.694	0.241	0.204	0.742	6.597	6.199	0.530
SJ14	0.003	0.005	0.191	0.953	0.797	0.351	0.000	1.295	0.139	0.624	0.035	0.035	3.651	0.470	5.073	0.081	0.013	3.322	0.139	0.090	0.129	8.326	0.129	0.166
SJ16	0.007	0.007	0.675	0.767	0.658	0.490	0.000	0.787	0.136	0.810	0.025	0.028	3.672	0.111	3.372	0.177	0.017	2.302	0.262	0.134	0.233	5.693	0.078	0.150
SJ19	0.008	0.008	0.378	0.603	0.839	0.469	0.001	1.111	0.176	0.685	0.100	0.041	4.089	0.187	6.478	0.188	0.027	1.221	0.212	0.157	0.097	6.468	0.032	0.124
SJ22	0.006	0.009	0.354	0.780	0.800	0.377	0.001	2.032	0.153	0.607	0.072	0.040	3.331	0.105	6.224	0.118	0.012	1.189	0.129	0.132	0.110	6.296	0.018	0.142

Table 8. Elemental enrichments by shale average

Average Shale [13]	Mn	Mg	Fe	Si	K	Ti	Ca	Na	Pb	Zr	P	Sr	Rb	U	Ba	Cu	Ni	As	V	Zn	Sb	Co	Mo	Cd
EST	0.558	1.771	0.994	4.388	2.560	1.342	29.461	0.262	5.219	1.432	3.803	5.414	1.065	3.114	0.900	0.527	0.987	2.138	1.043	0.357	0.407	1.142	0.986	1.017
UTH	0.670	6.797	1.399	4.662	2.083	0.691	21.519	2.538	2.008	0.741	0.846	11.172	1.392	3.667	2.751	0.880	0.511	13.047	1.127	0.943	1.447	2.471	2.960	1.809
URD	0.319	1.437	0.734	5.303	0.927	1.035	34.163	0.532	1.421	1.036	85.648	10.788	0.437	36.198	0.394	9.082	14.585	2.253	9.839	41.886	4.881	1.111	40.363	1078.770
C5	0.747	0.236	0.424	2.899	0.845	0.735	0.619	0.313	2.530	1.657	0.309	0.731	1.023	3.637	0.890	0.264	0.081	1.105	0.400	0.669	0.165	0.508	0.083	0.275
C8	2.269	0.296	1.333	3.241	0.939	0.594	2.395	0.325	2.975	1.468	0.491	1.477	1.090	5.679	1.211	0.441	0.172	3.819	0.616	0.843	0.525	0.975	0.298	0.438
C10	0.265	0.230	0.704	2.073	0.536	0.524	0.162	0.100	3.176	0.764	0.553	0.584	0.811	4.162	0.516	0.457	0.184	2.425	0.496	1.426	0.376	0.645	0.154	0.672
C12	1.187	0.174	0.545	2.148	0.566	0.524	0.124	0.090	2.462	0.767	0.428	0.565	0.792	2.654	0.606	0.317	0.112	1.981	0.470	1.410	0.320	0.495	0.081	0.458
C19	0.369	0.147	0.433	2.096	0.571	0.606	0.079	0.074	3.014	0.901	0.199	0.519	0.807	2.352	0.596	0.293	0.113	2.117	0.463	0.573	0.213	0.536	0.064	0.213
C22	0.058	0.128	0.409	2.894	0.775	0.825	0.068	0.174	3.487	2.079	0.194	0.620	0.938	2.924	0.996	0.280	0.124	1.712	0.461	1.327	0.363	0.635	0.113	0.389
C28	0.035	0.071	0.136	1.411	0.220	0.442	0.062	0.022	2.841	0.423	0.145	0.358	0.673	9.003	0.214	0.343	0.011	0.276	0.208	0.133	0.342	0.042	0.199	0.070
C29	0.095	0.067	0.948	1.266	0.121	0.218	0.167	0.020	19.686	0.325	0.722	0.736	0.371	85.778	7.343	0.318	0.110	3.991	0.891	2.223	1.974	0.522	1.065	2.146
C32	0.065	0.071	0.408	1.403	0.247	0.485	0.094	0.020	2.283	0.603	0.055	0.402	0.659	5.802	0.215	0.147	0.031	1.861	0.318	0.287	0.293	0.232	0.328	0.147
C33b	0.038	0.064	0.162	1.372	0.180	0.379	0.065	0.016	3.103	0.296	0.096	0.344	0.535	2.872	0.178	0.260	0.033	0.294	0.325	0.190	0.138	0.155	0.267	0.172
YC2	0.050	0.078	0.462	1.443	0.207	0.398	0.069	0.021	2.921	0.323	0.167	0.271	0.567	4.604	0.205	0.359	0.045	1.775	0.438	2.167	0.358	0.773	0.695	0.671
YC5	2.864	0.322	1.225	2.033	0.515	0.597	0.321	0.057	2.766	0.884	0.508	0.501	0.738	2.182	0.548	0.258	0.091	0.968	0.461	0.709	0.197	0.503	0.067	0.247
YC6	0.481	0.157	0.390	2.097	0.537	0.561	0.107	0.055	2.622	0.818	0.405	0.468	0.791	2.916	0.539	0.318	0.127	1.305	0.475	0.752	0.260	0.551	0.112	0.325
YC7	0.184	0.191	0.524	2.280	0.592	0.547	0.149	0.080	2.535	0.867	0.649	0.565	0.816	3.014	0.608	0.425	0.115	1.653	0.492	2.137	0.198	0.994	0.142	0.991
YC10	0.356	0.281	0.517	1.891	0.527	0.411	0.136	0.110	2.338	0.386	0.578	0.323	0.721	1.438	0.364	0.621	0.205	1.665	0.728	0.592	0.289	0.768	0.157	0.206
YC12	0.564	0.315	0.738	2.442	0.561	0.387	0.170	0.076	2.169	0.460	0.427	0.484	0.804	1.954	0.466	0.389	0.148	2.629	0.685	0.705	0.203	0.557	0.325	0.254
YC13	0.839	0.259	0.632	1.834	0.513	0.387	0.122	0.094	1.915	0.399	0.318	0.381	0.745	2.050	0.370	0.452	0.122	2.804	0.676	0.684	0.212	0.423	0.284	0.212
YC14	0.645	0.349	0.561	2.149	0.589	0.499	0.122	0.272	2.373	0.451	0.285	0.418	0.792	1.694	0.415	0.508	0.133	1.617	0.733	1.828	0.218	0.426	0.184	0.326
YC15	0.167	0.345	0.701	2.098	0.591	0.440	0.129	0.131	2.165	0.418	0.506	0.428	0.817	5.669	0.409	0.589	0.211	1.520	0.739	0.513	0.090	1.225	0.117	0.564
SJ2	0.614	0.525	0.653	4.686	1.425	0.844	3.158	1.106	1.487	1.603	0.698	1.670	1.368	1.782	1.937	0.315	0.326	1.120	0.526	0.445	0.332	0.648	0.057	0.207
SJ4	3.229	1.324	1.267	5.414	1.970	0.700	7.917	0.250	4.734	3.239	0.745	2.381	2.254	24.853	1.285	0.425	0.216	1.207	0.761	1.311	0.455	1.338	0.047	0.284
SJ6	0.681	0.819	0.785	3.923	1.350	0.892	1.824	1.583	2.509	1.486	1.032	1.494	1.547	23.097	1.646	0.446	0.300	2.443	0.836	1.046	0.276	0.882	0.009	0.345
SJ8	1.624	0.735	0.938	3.781	1.109	1.079	7.071	2.643	2.855	1.852	1.394	3.851	1.208	3.129	1.574	0.225	0.182	1.933	0.739	0.609	0.526	0.997	0.011	0.439
SJ10	0.154	0.488	1.088	3.017	0.962	0.727	0.215	0.116	3.246	0.980	0.349	0.901	1.465	9.620	0.689	0.619	0.331	6.899	0.733	1.957	0.498	1.116	0.476	1.246
SJ12	0.073	0.369	0.547	3.176	0.965	0.724	0.166	0.184	2.421	1.089	0.275	0.901	1.179	153.767	0.742	0.660	0.169	6.877	0.707	0.818	1.885	0.642	3.221	0.589
SJ14	0.091	0.307	0.295	5.969	1.540	0.661	0.119	1.027	1.188	1.412	0.384	1.363	1.490	5.323	1.666	0.137	0.071	4.867	0.407	0.363	0.328	0.810	0.067	0.185
SJ16	0.182	0.432	1.047	4.803	1.272	0.924	0.129	0.625	1.163	1.831	0.276	1.082	1.499	1.257	1.107	0.300	0.094	3.373	0.767	0.536	0.591	0.554	0.040	0.166
SJ19	0.227	0.466	0.586	3.776	1.621	0.884	0.184	0.881	1.512	1.549	1.089	1.581	1.669	2.112	2.127	0.319	0.150	1.789	0.622	0.629	0.245	0.629	0.017	0.138
SJ22	0.173	0.539	0.548	4.884	1.547	0.711	0.166	1.612	1.316	1.373	0.784	1.566	1.360	1.190	2.044	0.200	0.066	1.742	0.379	0.530	0.280	0.612	0.010	0.157

Table 9. Element enrichments by the Peruvian Marine average

Average Peru Marjin [14]	Mn	Mg	Fe	Si	K	Ti	Ca	Na	Pb	Zr	P	Sr	Rb	U	Ba	Cu	Ni	As	V	Zn	Sb	Co	Mo	Cd
EST	1.03	1.19	1.30	0.92	3.04	1.37	5.43	0.03	3.73	1.36	0.35	2.36	1.52	0.63	0.95	0.26	0.42	0.81	0.45	0.18	0.15	2.26	0.13	0.01
UTH	1.24	4.55	1.83	0.98	2.47	0.70	3.96	0.31	1.43	0.71	0.08	4.87	1.98	0.74	2.89	0.43	0.21	4.93	0.48	0.47	0.54	4.89	0.38	0.02
URD	0.59	0.96	0.96	1.12	1.10	1.06	6.29	0.07	1.02	0.99	7.81	4.70	0.62	7.28	0.41	4.40	6.14	0.85	4.21	20.72	1.83	2.20	5.24	9.52
C5	1.38	0.16	0.56	0.61	1.00	0.75	0.11	0.04	1.81	1.58	0.03	0.32	1.46	0.73	0.93	0.13	0.03	0.42	0.17	0.33	0.06	1.01	0.01	0.00
C8	4.19	0.20	1.75	0.68	1.11	0.61	0.44	0.04	2.12	1.40	0.04	0.64	1.55	1.14	1.27	0.21	0.07	1.44	0.26	0.42	0.20	1.93	0.04	0.00
C10	0.49	0.15	0.92	0.44	0.64	0.53	0.03	0.01	2.27	0.73	0.05	0.25	1.15	0.84	0.54	0.22	0.08	0.92	0.21	0.71	0.14	1.28	0.02	0.01
C12	2.19	0.12	0.72	0.45	0.67	0.53	0.02	0.01	1.76	0.73	0.04	0.25	1.13	0.53	0.64	0.15	0.05	0.75	0.20	0.70	0.12	0.98	0.01	0.00
C19	0.68	0.10	0.57	0.44	0.68	0.62	0.01	0.01	2.15	0.86	0.02	0.23	1.15	0.47	0.63	0.14	0.05	0.80	0.20	0.28	0.08	1.06	0.01	0.00
C22	0.11	0.09	0.54	0.61	0.92	0.84	0.01	0.02	2.49	1.98	0.02	0.27	1.34	0.59	1.05	0.14	0.05	0.65	0.20	0.66	0.14	1.26	0.01	0.00
C28	0.06	0.05	0.18	0.30	0.26	0.45	0.01	0.00	2.03	0.40	0.01	0.16	0.96	1.81	0.22	0.17	0.00	0.10	0.09	0.07	0.13	0.08	0.03	0.00
C29	0.18	0.05	1.24	0.27	0.14	0.22	0.03	0.00	14.06	0.31	0.07	0.32	0.53	17.25	7.72	0.15	0.05	1.51	0.38	1.10	0.74	1.03	0.14	0.02
C32	0.12	0.05	0.54	0.30	0.29	0.49	0.02	0.00	1.63	0.57	0.00	0.18	0.94	1.17	0.23	0.07	0.01	0.70	0.14	0.14	0.11	0.46	0.04	0.00
C33b	0.07	0.04	0.21	0.29	0.21	0.39	0.01	0.00	2.22	0.28	0.01	0.15	0.76	0.58	0.19	0.13	0.01	0.11	0.14	0.09	0.05	0.31	0.03	0.00
YC2	0.09	0.05	0.61	0.30	0.25	0.41	0.01	0.00	2.09	0.31	0.02	0.12	0.81	0.93	0.22	0.17	0.02	0.67	0.19	1.07	0.13	1.53	0.09	0.01
YC5	5.29	0.22	1.61	0.43	0.61	0.61	0.06	0.01	1.98	0.84	0.05	0.22	1.05	0.44	0.58	0.13	0.04	0.37	0.20	0.35	0.07	1.00	0.01	0.00
YC6	0.89	0.10	0.51	0.44	0.64	0.57	0.02	0.01	1.87	0.78	0.04	0.20	1.13	0.59	0.57	0.15	0.05	0.49	0.20	0.37	0.10	1.09	0.01	0.00
YC7	0.34	0.13	0.69	0.48	0.70	0.56	0.03	0.01	1.81	0.83	0.06	0.25	1.16	0.61	0.64	0.21	0.05	0.62	0.21	1.06	0.07	1.97	0.02	0.01
YC10	0.66	0.19	0.68	0.40	0.63	0.42	0.03	0.01	1.67	0.37	0.05	0.14	1.03	0.29	0.38	0.30	0.09	0.63	0.31	0.29	0.11	1.52	0.02	0.00
YC12	1.04	0.21	0.97	0.51	0.67	0.39	0.03	0.01	1.55	0.44	0.04	0.21	1.14	0.39	0.49	0.19	0.06	0.99	0.29	0.35	0.08	1.10	0.04	0.00
YC13	1.55	0.17	0.83	0.39	0.61	0.39	0.02	0.01	1.37	0.38	0.03	0.17	1.06	0.41	0.39	0.22	0.05	1.06	0.29	0.34	0.08	0.84	0.04	0.00
YC14	1.19	0.23	0.74	0.45	0.70	0.51	0.02	0.03	1.70	0.43	0.03	0.18	1.13	0.34	0.44	0.25	0.06	0.61	0.31	0.90	0.08	0.84	0.02	0.00
YC15	0.31	0.23	0.92	0.44	0.70	0.45	0.02	0.02	1.55	0.40	0.05	0.19	1.16	1.14	0.43	0.29	0.09	0.57	0.32	0.25	0.03	2.42	0.02	0.00
SJ2	1.13	0.35	0.86	0.99	1.69	0.86	0.58	0.14	1.06	1.53	0.06	0.73	1.95	0.36	2.04	0.15	0.14	0.42	0.23	0.22	0.12	1.28	0.01	0.00
SJ4	5.96	0.89	1.66	1.14	2.34	0.71	1.46	0.03	3.38	3.09	0.07	1.04	3.21	5.00	1.35	0.21	0.09	0.46	0.33	0.65	0.17	2.65	0.01	0.00
SJ6	1.26	0.55	1.03	0.83	1.60	0.91	0.34	0.19	1.79	1.42	0.09	0.65	2.20	4.64	1.73	0.22	0.13	0.92	0.36	0.52	0.10	1.75	0.00	0.00
SJ8	3.00	0.49	1.23	0.80	1.32	1.10	1.30	0.32	2.04	1.76	0.13	1.68	1.72	0.63	1.65	0.11	0.08	0.73	0.32	0.30	0.20	1.97	0.00	0.00
SJ10	0.28	0.33	1.43	0.64	1.14	0.74	0.04	0.01	2.32	0.93	0.03	0.39	2.08	1.93	0.72	0.30	0.14	2.61	0.31	0.97	0.19	2.21	0.06	0.01
SJ12	0.13	0.25	0.72	0.67	1.15	0.74	0.03	0.02	1.73	1.04	0.03	0.39	1.68	30.92	0.78	0.32	0.07	2.60	0.30	0.40	0.71	1.27	0.42	0.01
SJ14	0.17	0.21	0.39	1.26	1.83	0.67	0.02	0.13	0.85	1.35	0.03	0.59	2.12	1.07	1.75	0.07	0.03	1.84	0.17	0.18	0.12	1.60	0.01	0.00
SJ16	0.34	0.29	1.37	1.01	1.51	0.94	0.02	0.08	0.83	1.74	0.03	0.47	2.13	0.25	1.16	0.15	0.04	1.27	0.33	0.27	0.22	1.10	0.01	0.00
SJ19	0.42	0.31	0.77	0.80	1.93	0.90	0.03	0.11	1.08	1.47	0.10	0.69	2.37	0.42	2.24	0.15	0.06	0.68	0.27	0.31	0.09	1.25	0.00	0.00
SJ22	0.32	0.36	0.72	1.03	1.84	0.73	0.03	0.20	0.94	1.31	0.07	0.68	1.93	0.24	2.15	0.10	0.03	0.66	0.16	0.26	0.10	1.21	0.00	0.00

Table 10. Element enrichments by Namibian Mud Lens average

Namibian Mud Lenses [15]	Mn	Mg	Fe	Si	K	Ti	Ca	Na	Pb	Zr	P	Sr	Rb	U	Ba	Cu	Ni	As	V	Zn	Co	Mo	Cd
EST	1.91	0.87	0.73	0.13	2.18	0.89	4.07	0.03	3.53	1.14	0.20	1.12	0.85	0.05	0.22	0.09	0.20	0.32	0.13	0.15	0.93	0.04	0.00
UTH	2.30	3.35	1.03	0.14	1.78	0.46	2.97	0.33	1.36	0.59	0.04	2.31	1.11	0.06	0.67	0.15	0.11	1.93	0.15	0.39	2.02	0.11	0.01
URD	1.09	0.71	0.54	0.16	0.79	0.69	4.72	0.07	0.96	0.82	4.41	2.24	0.35	0.59	0.10	1.60	3.02	0.33	1.27	17.15	0.91	1.50	3.11
C5	2.56	0.12	0.31	0.09	0.72	0.49	0.09	0.04	1.71	1.32	0.02	0.15	0.81	0.06	0.22	0.05	0.02	0.16	0.05	0.27	0.42	0.00	0.00
C8	7.78	0.15	0.98	0.10	0.80	0.39	0.33	0.04	2.01	1.17	0.03	0.31	0.87	0.09	0.29	0.08	0.04	0.56	0.08	0.35	0.80	0.01	0.00
C10	0.91	0.11	0.52	0.06	0.46	0.35	0.02	0.01	2.15	0.61	0.03	0.12	0.64	0.07	0.13	0.08	0.04	0.36	0.06	0.58	0.53	0.01	0.00
C12	4.07	0.09	0.40	0.06	0.48	0.35	0.02	0.01	1.66	0.61	0.02	0.12	0.63	0.04	0.15	0.06	0.02	0.29	0.06	0.58	0.41	0.00	0.00
C19	1.26	0.07	0.32	0.06	0.49	0.40	0.01	0.01	2.04	0.72	0.01	0.11	0.64	0.04	0.14	0.05	0.02	0.31	0.06	0.23	0.44	0.00	0.00
C22	0.20	0.06	0.30	0.09	0.66	0.55	0.01	0.02	2.36	1.65	0.01	0.13	0.75	0.05	0.24	0.05	0.03	0.25	0.06	0.54	0.52	0.00	0.00
C28	0.12	0.04	0.10	0.04	0.19	0.29	0.01	0.00	1.92	0.34	0.01	0.07	0.54	0.15	0.05	0.06	0.00	0.04	0.03	0.05	0.03	0.01	0.00
C29	0.33	0.03	0.70	0.04	0.10	0.14	0.02	0.00	13.30	0.26	0.04	0.15	0.29	1.39	1.79	0.06	0.02	0.59	0.11	0.91	0.43	0.04	0.01
C32	0.22	0.03	0.30	0.04	0.21	0.32	0.01	0.00	1.54	0.48	0.00	0.08	0.52	0.09	0.05	0.03	0.01	0.27	0.04	0.12	0.19	0.01	0.00
C33b	0.13	0.03	0.12	0.04	0.15	0.25	0.01	0.00	2.10	0.23	0.00	0.07	0.43	0.05	0.04	0.05	0.01	0.04	0.04	0.08	0.13	0.01	0.00
YC2	0.17	0.04	0.34	0.04	0.18	0.26	0.01	0.00	1.97	0.26	0.01	0.06	0.45	0.07	0.05	0.06	0.01	0.26	0.06	0.89	0.63	0.03	0.00
YC5	9.82	0.16	0.90	0.06	0.44	0.40	0.04	0.01	1.87	0.70	0.03	0.10	0.59	0.04	0.13	0.05	0.02	0.14	0.06	0.29	0.41	0.00	0.00
YC6	1.65	0.08	0.29	0.06	0.46	0.37	0.01	0.01	1.77	0.65	0.02	0.10	0.63	0.05	0.13	0.06	0.03	0.19	0.06	0.31	0.45	0.00	0.00
YC7	0.63	0.09	0.39	0.07	0.50	0.36	0.02	0.01	1.71	0.69	0.03	0.12	0.65	0.05	0.15	0.07	0.02	0.24	0.06	0.87	0.81	0.01	0.00
YC10	1.22	0.14	0.38	0.06	0.45	0.27	0.02	0.01	1.58	0.31	0.03	0.07	0.57	0.02	0.09	0.11	0.04	0.25	0.09	0.24	0.63	0.01	0.00
YC12	1.93	0.16	0.54	0.07	0.48	0.26	0.02	0.01	1.47	0.37	0.02	0.10	0.64	0.03	0.11	0.07	0.03	0.39	0.09	0.29	0.46	0.01	0.00
YC13	2.88	0.13	0.47	0.06	0.44	0.26	0.02	0.01	1.29	0.32	0.02	0.08	0.59	0.03	0.09	0.08	0.03	0.41	0.09	0.28	0.35	0.01	0.00
YC14	2.21	0.17	0.41	0.06	0.50	0.33	0.02	0.04	1.60	0.36	0.01	0.09	0.63	0.03	0.10	0.09	0.03	0.24	0.09	0.75	0.35	0.01	0.00
YC15	0.57	0.17	0.52	0.06	0.50	0.29	0.02	0.02	1.46	0.33	0.03	0.09	0.65	0.09	0.10	0.10	0.04	0.22	0.10	0.21	1.00	0.00	0.00
SJ2	2.11	0.26	0.48	0.14	1.21	0.56	0.44	0.15	1.00	1.27	0.04	0.35	1.09	0.03	0.47	0.06	0.07	0.17	0.07	0.18	0.53	0.00	0.00
SJ4	11.07	0.65	0.93	0.16	1.68	0.46	1.09	0.03	3.20	2.57	0.04	0.49	1.79	0.40	0.31	0.07	0.04	0.18	0.10	0.54	1.10	0.00	0.00
SJ6	2.34	0.40	0.58	0.12	1.15	0.59	0.25	0.21	1.70	1.18	0.05	0.31	1.23	0.37	0.40	0.08	0.06	0.36	0.11	0.43	0.72	0.00	0.00
SJ8	5.57	0.36	0.69	0.11	0.95	0.71	0.98	0.35	1.93	1.47	0.07	0.80	0.96	0.05	0.38	0.04	0.04	0.29	0.10	0.25	0.82	0.00	0.00

Table 11. Element enrichments by Mediterranean Sapropel average

Mediterranean Sapropels [16]	Mn	Mg	Fe	Si	K	Ti	Ca	Na	Pb	Zr	P	Sr	Rb	U	Ba	Cu	Ni	As	V	Zn	Sb	Co	Mo	Cd
EST	0.27	0.85	0.48	1.51	3.40	1.17	2.00	0.07	4.50	1.19	2.08	1.02	1.54	0.35	0.19	0.09	0.15	0.23	0.12	0.17	0.03	0.16	0.05	0.03
UTH	0.32	3.27	0.68	1.61	2.77	0.60	1.46	0.68	1.73	0.62	0.46	2.09	2.01	0.41	0.58	0.15	0.08	1.38	0.13	0.45	0.10	0.34	0.15	0.05
URD	0.15	0.69	0.35	1.83	1.23	0.90	2.32	0.14	1.23	0.86	46.84	2.02	0.63	4.08	0.08	1.54	2.27	0.24	1.15	19.90	0.34	0.15	1.99	29.97
C5	0.36	0.11	0.21	1.00	1.12	0.64	0.04	0.08	2.18	1.38	0.17	0.14	1.48	0.41	0.19	0.04	0.01	0.12	0.05	0.32	0.01	0.07	0.00	0.01
C8	1.08	0.14	0.64	1.12	1.25	0.52	0.16	0.09	2.56	1.22	0.27	0.28	1.58	0.64	0.26	0.07	0.03	0.40	0.07	0.40	0.04	0.13	0.01	0.01
C10	0.13	0.11	0.34	0.71	0.71	0.46	0.01	0.03	2.74	0.64	0.30	0.11	1.17	0.47	0.11	0.08	0.03	0.26	0.06	0.68	0.03	0.09	0.01	0.02
C12	0.56	0.08	0.26	0.74	0.75	0.46	0.01	0.02	2.12	0.64	0.23	0.11	1.15	0.30	0.13	0.05	0.02	0.21	0.05	0.67	0.02	0.07	0.00	0.01
C19	0.18	0.07	0.21	0.72	0.76	0.53	0.01	0.02	2.60	0.75	0.11	0.10	1.17	0.27	0.13	0.05	0.02	0.22	0.05	0.27	0.01	0.07	0.00	0.01
C22	0.03	0.06	0.20	1.00	1.03	0.72	0.00	0.05	3.01	1.73	0.11	0.12	1.36	0.33	0.21	0.05	0.02	0.18	0.05	0.63	0.03	0.09	0.01	0.01
C28	0.02	0.03	0.07	0.49	0.29	0.38	0.00	0.01	2.45	0.35	0.08	0.07	0.97	1.02	0.05	0.06	0.00	0.03	0.02	0.06	0.02	0.01	0.01	0.00
C29	0.05	0.03	0.46	0.44	0.16	0.19	0.01	0.01	16.97	0.27	0.40	0.14	0.54	9.68	1.56	0.05	0.02	0.42	0.10	1.06	0.14	0.07	0.05	0.06
C32	0.03	0.03	0.20	0.48	0.33	0.42	0.01	0.01	1.97	0.50	0.03	0.08	0.95	0.65	0.05	0.02	0.00	0.20	0.04	0.14	0.02	0.03	0.02	0.00
C33b	0.02	0.03	0.08	0.47	0.24	0.33	0.00	0.00	2.68	0.25	0.05	0.06	0.77	0.32	0.04	0.04	0.01	0.03	0.04	0.09	0.01	0.02	0.01	0.00
YC2	0.02	0.04	0.22	0.50	0.28	0.35	0.00	0.01	2.52	0.27	0.09	0.05	0.82	0.52	0.04	0.06	0.01	0.19	0.05	1.03	0.03	0.11	0.03	0.02
YC5	1.36	0.15	0.59	0.70	0.69	0.52	0.02	0.02	2.38	0.74	0.28	0.09	1.07	0.25	0.12	0.04	0.01	0.10	0.05	0.34	0.01	0.07	0.00	0.01
YC6	0.23	0.08	0.19	0.72	0.71	0.49	0.01	0.01	2.26	0.68	0.22	0.09	1.14	0.33	0.11	0.05	0.02	0.14	0.06	0.36	0.02	0.08	0.01	0.01
YC7	0.09	0.09	0.25	0.79	0.79	0.47	0.01	0.02	2.19	0.72	0.35	0.11	1.18	0.34	0.13	0.07	0.02	0.17	0.06	1.01	0.01	0.14	0.01	0.03
YC10	0.17	0.14	0.25	0.65	0.70	0.36	0.01	0.03	2.02	0.32	0.32	0.06	1.04	0.16	0.08	0.11	0.03	0.18	0.09	0.28	0.02	0.10	0.01	0.01
YC12	0.27	0.15	0.36	0.84	0.75	0.34	0.01	0.02	1.87	0.38	0.23	0.09	1.16	0.22	0.10	0.07	0.02	0.28	0.08	0.33	0.01	0.08	0.02	0.01
YC13	0.40	0.12	0.31	0.63	0.68	0.34	0.01	0.02	1.65	0.33	0.17	0.07	1.08	0.23	0.08	0.08	0.02	0.30	0.08	0.33	0.01	0.06	0.01	0.01
YC14	0.31	0.17	0.27	0.74	0.78	0.43	0.01	0.07	2.05	0.38	0.16	0.08	1.15	0.19	0.09	0.09	0.02	0.17	0.09	0.87	0.02	0.06	0.01	0.01
YC15	0.08	0.17	0.34	0.72	0.79	0.38	0.01	0.03	1.87	0.35	0.28	0.08	1.18	0.64	0.09	0.10	0.03	0.16	0.09	0.24	0.01	0.17	0.01	0.02
SJ2	0.29	0.25	0.32	1.61	1.90	0.73	0.21	0.29	1.28	1.34	0.38	0.31	1.98	0.20	0.41	0.05	0.05	0.12	0.06	0.21	0.02	0.09	0.00	0.01
SJ4	1.53	0.64	0.61	1.86	2.62	0.61	0.54	0.07	4.08	2.70	0.41	0.45	3.26	2.80	0.27	0.07	0.03	0.13	0.09	0.62	0.03	0.18	0.00	0.01
SJ6	0.32	0.39	0.38	1.35	1.80	0.78	0.12	0.42	2.16	1.24	0.56	0.28	2.24	2.61	0.35	0.08	0.05	0.26	0.10	0.50	0.02	0.12	0.00	0.01
SJ8	0.77	0.35	0.45	1.30	1.47	0.94	0.48	0.70	2.46	1.54	0.76	0.72	1.75	0.35	0.33	0.04	0.03	0.20	0.09	0.29	0.04	0.14	0.00	0.01
SJ10	0.07	0.23	0.53	1.04	1.28	0.63	0.01	0.03	2.80	0.82	0.19	0.17	2.12	1.09	0.15	0.11	0.05	0.73	0.09	0.93	0.03	0.15	0.02	0.03
SJ12	0.03	0.18	0.26	1.09	1.28	0.63	0.01	0.05	2.09	0.91	0.15	0.17	1.70	17.35	0.16	0.11	0.03	0.73	0.08	0.39	0.13	0.09	0.16	0.02
SJ14	0.04	0.15	0.14	2.06	2.05	0.57	0.01	0.27	1.02	1.18	0.21	0.26	2.16	0.60	0.35	0.02	0.01	0.51	0.05	0.17	0.02	0.11	0.00	0.01
SJ16	0.09	0.21	0.51	1.65	1.69	0.80	0.01	0.17	1.00	1.53	0.15	0.20	2.17	0.14	0.24	0.05	0.01	0.36	0.09	0.25	0.04	0.08	0.00	0.00
SJ19	0.11	0.22	0.28	1.30	2.16	0.77	0.01	0.23	1.30	1.29	0.60	0.30	2.41	0.24	0.45	0.05	0.02	0.19	0.07	0.30	0.02	0.09	0.00	0.00
SJ22	0.08	0.26	0.27	1.68	2.06	0.62	0.01	0.43	1.13	1.14	0.43	0.29	1.97	0.13	0.43	0.03	0.01	0.18	0.04	0.25	0.02	0.08	0.00	0.00

Table 12. Element enrichments by Black Sea Sapropel average

Black Sea Sapropels [17]	Mn	Mg	Fe	Si	K	Ti	Ca	Na	Pb	Zr	P	Sr	Rb	U	Ba	Cu	Ni	As	V	Zn	Sb	Co	Mo	Cd
EST	0.42	1.11	0.90	1.30	2.84	1.48	1.58	0.03	2.46	1.59	1.85	0.75	1.19	0.45	0.37	0.17	0.50	0.84	0.58	0.22	0.13	0.44	0.09	0.29
UTH	0.50	4.25	1.27	1.38	2.31	0.76	1.15	0.31	0.95	0.82	0.41	1.55	1.56	0.53	1.15	0.28	0.26	5.11	0.63	0.59	0.48	0.95	0.28	0.52
URD	0.24	0.90	0.67	1.57	1.03	1.14	1.83	0.07	0.67	1.15	41.63	1.49	0.49	5.23	0.16	2.90	7.42	0.88	5.51	26.18	1.61	0.43	3.78	311.18
C5	0.56	0.15	0.39	0.86	0.94	0.81	0.03	0.04	1.19	1.84	0.15	0.10	1.15	0.53	0.37	0.08	0.04	0.43	0.22	0.42	0.05	0.19	0.01	0.08
C8	1.69	0.18	1.21	0.96	1.04	0.66	0.13	0.04	1.40	1.63	0.24	0.20	1.22	0.82	0.50	0.14	0.09	1.50	0.35	0.53	0.17	0.37	0.03	0.13
C10	0.20	0.14	0.64	0.61	0.59	0.58	0.01	0.01	1.50	0.85	0.27	0.08	0.91	0.60	0.21	0.15	0.09	0.95	0.28	0.89	0.12	0.25	0.01	0.19
C12	0.88	0.11	0.50	0.64	0.63	0.58	0.01	0.01	1.16	0.85	0.21	0.08	0.89	0.38	0.25	0.10	0.06	0.78	0.26	0.88	0.11	0.19	0.01	0.13
C19	0.27	0.09	0.39	0.62	0.63	0.67	0.00	0.01	1.42	1.00	0.10	0.07	0.91	0.34	0.25	0.09	0.06	0.83	0.26	0.36	0.07	0.21	0.01	0.06
C22	0.04	0.08	0.37	0.86	0.86	0.91	0.00	0.02	1.64	2.31	0.09	0.09	1.05	0.42	0.41	0.09	0.06	0.67	0.26	0.83	0.12	0.24	0.01	0.11
C28	0.03	0.04	0.12	0.42	0.24	0.49	0.00	0.00	1.34	0.47	0.07	0.05	0.75	1.30	0.09	0.11	0.01	0.11	0.12	0.08	0.11	0.02	0.02	0.02
C29	0.07	0.04	0.86	0.37	0.13	0.24	0.01	0.00	9.29	0.36	0.35	0.10	0.42	12.40	3.06	0.10	0.06	1.56	0.50	1.39	0.65	0.20	0.10	0.62
C32	0.05	0.04	0.37	0.42	0.27	0.54	0.01	0.00	1.08	0.67	0.03	0.06	0.74	0.84	0.09	0.05	0.02	0.73	0.18	0.18	0.10	0.09	0.03	0.04
C33b	0.03	0.04	0.15	0.41	0.20	0.42	0.00	0.00	1.46	0.33	0.05	0.05	0.60	0.42	0.07	0.08	0.02	0.11	0.18	0.12	0.05	0.06	0.03	0.05
YC2	0.04	0.05	0.42	0.43	0.23	0.44	0.00	0.00	1.38	0.36	0.08	0.04	0.64	0.67	0.09	0.11	0.02	0.69	0.25	1.35	0.12	0.30	0.07	0.19
YC5	2.13	0.20	1.11	0.60	0.57	0.66	0.02	0.01	1.30	0.98	0.25	0.07	0.83	0.32	0.23	0.08	0.05	0.38	0.26	0.44	0.06	0.19	0.01	0.07
YC6	0.36	0.10	0.35	0.62	0.60	0.62	0.01	0.01	1.24	0.91	0.20	0.06	0.89	0.42	0.22	0.10	0.06	0.51	0.27	0.47	0.09	0.21	0.01	0.09
YC7	0.14	0.12	0.48	0.68	0.66	0.60	0.01	0.01	1.20	0.96	0.32	0.08	0.92	0.44	0.25	0.14	0.06	0.65	0.28	1.34	0.07	0.38	0.01	0.29
YC10	0.27	0.18	0.47	0.56	0.58	0.45	0.01	0.01	1.10	0.43	0.28	0.04	0.81	0.21	0.15	0.20	0.10	0.65	0.41	0.37	0.09	0.29	0.01	0.06
YC12	0.42	0.20	0.67	0.72	0.62	0.43	0.01	0.01	1.02	0.51	0.21	0.07	0.90	0.28	0.19	0.12	0.08	1.03	0.38	0.44	0.07	0.21	0.03	0.07
YC13	0.62	0.16	0.57	0.54	0.57	0.43	0.01	0.01	0.90	0.44	0.15	0.05	0.84	0.30	0.15	0.14	0.06	1.10	0.38	0.43	0.07	0.16	0.03	0.06
YC14	0.48	0.22	0.51	0.64	0.65	0.55	0.01	0.03	1.12	0.50	0.14	0.06	0.89	0.24	0.17	0.16	0.07	0.63	0.41	1.14	0.07	0.16	0.02	0.09
YC15	0.12	0.22	0.64	0.62	0.66	0.49	0.01	0.02	1.02	0.46	0.25	0.06	0.92	0.82	0.17	0.19	0.11	0.60	0.41	0.32	0.03	0.47	0.01	0.16
SJ2	0.46	0.33	0.59	1.39	1.58	0.93	0.17	0.14	0.70	1.78	0.34	0.23	1.54	0.26	0.81	0.10	0.17	0.44	0.29	0.28	0.11	0.25	0.01	0.06
SJ4	2.40	0.83	1.15	1.60	2.18	0.77	0.42	0.03	2.23	3.60	0.36	0.33	2.53	3.59	0.54	0.14	0.11	0.47	0.43	0.82	0.15	0.51	0.00	0.08
SJ6	0.51	0.51	0.71	1.16	1.50	0.99	0.10	0.19	1.18	1.65	0.50	0.21	1.74	3.34	0.69	0.14	0.15	0.96	0.47	0.65	0.09	0.34	0.00	0.10
SJ8	1.21	0.46	0.85	1.12	1.23	1.19	0.38	0.32	1.35	2.06	0.68	0.53	1.36	0.45	0.66	0.07	0.09	0.76	0.41	0.38	0.17	0.38	0.00	0.13
SJ10	0.11	0.31	0.99	0.89	1.07	0.80	0.01	0.01	1.53	1.09	0.17	0.12	1.64	1.39	0.29	0.20	0.17	2.70	0.41	1.22	0.16	0.43	0.04	0.36
SJ12	0.05	0.23	0.50	0.94	1.07	0.80	0.01	0.02	1.14	1.21	0.13	0.12	1.32	22.22	0.31	0.21	0.09	2.69	0.40	0.51	0.62	0.25	0.30	0.17
SJ14	0.07	0.19	0.27	1.77	1.71	0.73	0.01	0.13	0.56	1.57	0.19	0.19	1.67	0.77	0.69	0.04	0.04	1.91	0.23	0.23	0.11	0.31	0.01	0.05
SJ16	0.14	0.27	0.95	1.42	1.41	1.02	0.01	0.08	0.55	2.03	0.13	0.15	1.68	0.18	0.46	0.10	0.05	1.32	0.43	0.34	0.19	0.21	0.00	0.05
SJ19	0.17	0.29	0.53	1.12	1.80	0.98	0.01	0.11	0.71	1.72	0.53	0.22	1.87	0.31	0.89	0.10	0.08	0.70	0.35	0.39	0.08	0.24	0.00	0.04
SJ22	0.13	0.34	0.50	1.45	1.72	0.79	0.01	0.20	0.62	1.53	0.38	0.22	1.53	0.17	0.85	0.06	0.03	0.68	0.21	0.33	0.09	0.23	0.00	0.05

Table 13. Element enrichments according to the C/T Demerara Rise average

C/T Demerara Rise [18]	Mn	Mg	Fe	Si	K	Ti	Ca	Na	Pb	Zr	P	Sr	Rb	U	Ba	Cu	Ni	As	V	Zn	Sb	Co	Mo	Cd
EST	1.27	1.38	0.95	0.65	3.27	1.34	0.95	0.08	4.35	1.91	0.48	0.64	1.66	0.30	0.42	0.09	0.14	0.40	0.03	0.02	0.02	0.96	0.04	0.01
UTH	1.53	5.31	1.33	0.69	2.66	0.69	0.69	0.74	1.67	0.99	0.11	1.32	2.17	0.35	1.29	0.16	0.07	2.47	0.04	0.05	0.06	2.09	0.11	0.02
URD	0.73	1.12	0.70	0.79	1.19	1.04	1.10	0.16	1.18	1.38	10.71	1.27	0.68	3.44	0.18	1.60	2.07	0.43	0.33	2.02	0.21	0.94	1.47	13.93
C5	1.71	0.18	0.40	0.43	1.08	0.74	0.02	0.09	2.11	2.21	0.04	0.09	1.60	0.35	0.42	0.05	0.01	0.21	0.01	0.03	0.01	0.43	0.00	0.00
C8	5.19	0.23	1.27	0.48	1.20	0.59	0.08	0.10	2.48	1.96	0.06	0.17	1.70	0.54	0.57	0.08	0.02	0.72	0.02	0.04	0.02	0.82	0.01	0.01
C10	0.61	0.18	0.67	0.31	0.69	0.52	0.01	0.03	2.65	1.02	0.07	0.07	1.27	0.40	0.24	0.08	0.03	0.46	0.02	0.07	0.02	0.55	0.01	0.01
C12	2.71	0.14	0.52	0.32	0.72	0.52	0.00	0.03	2.05	1.02	0.05	0.07	1.24	0.25	0.28	0.06	0.02	0.37	0.02	0.07	0.01	0.42	0.00	0.01
C19	0.84	0.11	0.41	0.31	0.73	0.61	0.00	0.02	2.51	1.20	0.02	0.06	1.26	0.22	0.28	0.05	0.02	0.40	0.02	0.03	0.01	0.45	0.00	0.00
C22	0.13	0.10	0.39	0.43	0.99	0.83	0.00	0.05	2.91	2.77	0.02	0.07	1.47	0.28	0.47	0.05	0.02	0.32	0.02	0.06	0.02	0.54	0.00	0.01
C28	0.08	0.06	0.13	0.21	0.28	0.44	0.00	0.01	2.37	0.56	0.02	0.04	1.05	0.85	0.10	0.06	0.00	0.05	0.01	0.01	0.01	0.04	0.01	0.00
C29	0.22	0.05	0.90	0.19	0.15	0.22	0.01	0.01	16.41	0.43	0.09	0.09	0.58	8.15	3.43	0.06	0.02	0.75	0.03	0.11	0.08	0.44	0.04	0.03
C32	0.15	0.06	0.39	0.21	0.32	0.49	0.00	0.01	1.90	0.80	0.01	0.05	1.03	0.55	0.10	0.03	0.00	0.35	0.01	0.01	0.01	0.20	0.01	0.00
C33b	0.09	0.05	0.15	0.20	0.23	0.38	0.00	0.00	2.59	0.39	0.01	0.04	0.84	0.27	0.08	0.05	0.00	0.06	0.01	0.01	0.01	0.13	0.01	0.00
YC2	0.11	0.06	0.44	0.21	0.26	0.40	0.00	0.01	2.43	0.43	0.02	0.03	0.89	0.44	0.10	0.06	0.01	0.34	0.01	0.10	0.02	0.65	0.03	0.01
YC5	6.55	0.25	1.17	0.30	0.66	0.60	0.01	0.02	2.31	1.18	0.06	0.06	1.15	0.21	0.26	0.05	0.01	0.18	0.02	0.03	0.01	0.42	0.00	0.00
YC6	1.10	0.12	0.37	0.31	0.69	0.56	0.00	0.02	2.19	1.09	0.05	0.06	1.24	0.28	0.25	0.06	0.02	0.25	0.02	0.04	0.01	0.47	0.00	0.00
YC7	0.42	0.15	0.50	0.34	0.76	0.55	0.00	0.02	2.11	1.16	0.08	0.07	1.28	0.29	0.28	0.07	0.02	0.31	0.02	0.10	0.01	0.84	0.01	0.01
YC10	0.81	0.22	0.49	0.28	0.67	0.41	0.00	0.03	1.95	0.51	0.07	0.04	1.13	0.14	0.17	0.11	0.03	0.31	0.02	0.03	0.01	0.65	0.01	0.00
YC12	1.29	0.25	0.70	0.36	0.72	0.39	0.01	0.02	1.81	0.61	0.05	0.06	1.26	0.19	0.22	0.07	0.02	0.50	0.02	0.03	0.01	0.47	0.01	0.00
YC13	1.92	0.20	0.60	0.27	0.66	0.39	0.00	0.03	1.60	0.53	0.04	0.04	1.16	0.19	0.17	0.08	0.02	0.53	0.02	0.03	0.01	0.36	0.01	0.00
YC14	1.47	0.27	0.53	0.32	0.75	0.50	0.00	0.08	1.98	0.60	0.04	0.05	1.24	0.16	0.19	0.09	0.02	0.31	0.02	0.09	0.01	0.36	0.01	0.00
YC15	0.38	0.27	0.67	0.31	0.76	0.44	0.00	0.04	1.80	0.56	0.06	0.05	1.28	0.54	0.19	0.10	0.03	0.29	0.02	0.02	0.00	1.04	0.00	0.01
SJ2	1.40	0.41	0.62	0.70	1.82	0.84	0.10	0.32	1.24	2.14	0.09	0.20	2.14	0.17	0.91	0.06	0.05	0.21	0.02	0.02	0.01	0.55	0.00	0.00
SJ4	7.38	1.03	1.21	0.81	2.52	0.70	0.26	0.07	3.95	4.32	0.09	0.28	3.52	2.36	0.60	0.07	0.03	0.23	0.03	0.06	0.02	1.13	0.00	0.00
SJ6	1.56	0.64	0.75	0.58	1.73	0.89	0.06	0.46	2.09	1.98	0.13	0.18	2.42	2.19	0.77	0.08	0.04	0.46	0.03	0.05	0.01	0.75	0.00	0.00
SJ8	3.71	0.57	0.89	0.56	1.42	1.08	0.23	0.77	2.38	2.47	0.17	0.45	1.89	0.30	0.74	0.04	0.03	0.37	0.02	0.03	0.02	0.84	0.00	0.01
SJ10	0.35	0.38	1.04	0.45	1.23	0.73	0.01	0.03	2.71	1.31	0.04	0.11	2.29	0.91	0.32	0.11	0.05	1.30	0.02	0.09	0.02	0.94	0.02	0.02
SJ12	0.17	0.29	0.52	0.47	1.23	0.72	0.01	0.05	2.02	1.45	0.03	0.11	1.84	14.60	0.35	0.12	0.02	1.30	0.02	0.04	0.08	0.54	0.12	0.01
SJ14	0.21	0.24	0.28	0.89	1.97	0.66	0.00	0.30	0.99	1.88	0.05	0.16	2.33	0.51	0.78	0.02	0.01	0.92	0.01	0.02	0.01	0.68	0.00	0.00
SJ16	0.42	0.34	1.00	0.71	1.63	0.92	0.00	0.18	0.97	2.44	0.03	0.13	2.34	0.12	0.52	0.05	0.01	0.64	0.03	0.03	0.03	0.47	0.00	0.00
SJ19	0.52	0.36	0.56	0.56	2.07	0.88	0.01	0.26	1.26	2.06	0.14	0.19	2.61	0.20	1.00	0.06	0.02	0.34	0.02	0.03	0.01	0.53	0.00	0.00
SJ22	0.39	0.42	0.52	0.73	1.98	0.71	0.01	0.47	1.10	1.83	0.10	0.18	2.12	0.11	0.96	0.04	0.01	0.33	0.01	0.03	0.01	0.52	0.00	0.00

Table 14. Element enrichments according to C/T Gubbio average

C/T Gubbio [18]	Mn	Mg	Fe	Si	K	Ti	Ca	Na	Pb	Zr	P	Sr	Rb	U	Ba	Cu	Ni	As	V	Zn	Sb	Co	Mo	Cd
EST	2.33	1.44	0.44	0.24	2.30	1.62	36.99	0.63	0.78	1.51	0.72	1.66	1.12	0.50	0.02	0.05	0.16	0.19	0.06	0.02	0.05	0.46	0.11	0.04
UTH	2.80	5.54	0.62	0.26	1.87	0.83	27.02	6.09	0.30	0.78	0.16	3.43	1.46	0.58	0.05	0.08	0.08	1.18	0.07	0.04	0.17	0.99	0.32	0.06
URD	1.33	1.17	0.33	0.30	0.83	1.25	42.90	1.28	0.21	1.09	16.29	3.32	0.46	5.77	0.01	0.81	2.37	0.20	0.59	2.00	0.59	0.45	4.34	37.81
C5	3.12	0.19	0.19	0.16	0.76	0.89	0.78	0.75	0.38	1.74	0.06	0.22	1.07	0.58	0.02	0.02	0.01	0.10	0.02	0.03	0.02	0.20	0.01	0.01
C8	9.47	0.24	0.59	0.18	0.84	0.72	3.01	0.78	0.45	1.55	0.09	0.45	1.14	0.91	0.02	0.04	0.03	0.34	0.04	0.04	0.06	0.39	0.03	0.02
C10	1.11	0.19	0.31	0.12	0.48	0.63	0.20	0.24	0.48	0.80	0.11	0.18	0.85	0.66	0.01	0.04	0.03	0.22	0.03	0.07	0.05	0.26	0.02	0.02
C12	4.95	0.14	0.24	0.12	0.51	0.63	0.16	0.22	0.37	0.81	0.08	0.17	0.83	0.42	0.01	0.03	0.02	0.18	0.03	0.07	0.04	0.20	0.01	0.02
C19	1.54	0.12	0.19	0.12	0.51	0.73	0.10	0.18	0.45	0.95	0.04	0.16	0.85	0.38	0.01	0.03	0.02	0.19	0.03	0.03	0.03	0.22	0.01	0.01
C22	0.24	0.10	0.18	0.16	0.70	0.99	0.09	0.42	0.52	2.19	0.04	0.19	0.98	0.47	0.02	0.03	0.02	0.15	0.03	0.06	0.04	0.26	0.01	0.01
C28	0.14	0.06	0.06	0.08	0.20	0.53	0.08	0.05	0.43	0.45	0.03	0.11	0.71	1.44	0.00	0.03	0.00	0.02	0.01	0.01	0.04	0.02	0.02	0.00
C29	0.40	0.05	0.42	0.07	0.11	0.26	0.21	0.05	2.95	0.34	0.14	0.23	0.39	13.68	0.15	0.03	0.02	0.36	0.05	0.11	0.24	0.21	0.11	0.08
C32	0.27	0.06	0.18	0.08	0.22	0.58	0.12	0.05	0.34	0.63	0.01	0.12	0.69	0.93	0.00	0.01	0.01	0.17	0.02	0.01	0.04	0.09	0.04	0.01
C33b	0.16	0.05	0.07	0.08	0.16	0.46	0.08	0.04	0.46	0.31	0.02	0.11	0.56	0.46	0.00	0.02	0.01	0.03	0.02	0.01	0.02	0.06	0.03	0.01
YC2	0.21	0.06	0.20	0.08	0.19	0.48	0.09	0.05	0.44	0.34	0.03	0.08	0.59	0.73	0.00	0.03	0.01	0.16	0.03	0.10	0.04	0.31	0.07	0.02
YC5	11.95	0.26	0.54	0.11	0.46	0.72	0.40	0.14	0.41	0.93	0.10	0.15	0.77	0.35	0.01	0.02	0.01	0.09	0.03	0.03	0.02	0.20	0.01	0.01
YC6	2.01	0.13	0.17	0.12	0.48	0.68	0.13	0.13	0.39	0.86	0.08	0.14	0.83	0.46	0.01	0.03	0.02	0.12	0.03	0.04	0.03	0.22	0.01	0.01
YC7	0.77	0.16	0.23	0.13	0.53	0.66	0.19	0.19	0.38	0.91	0.12	0.17	0.86	0.48	0.01	0.04	0.02	0.15	0.03	0.10	0.02	0.40	0.02	0.03
YC10	1.49	0.23	0.23	0.11	0.47	0.50	0.17	0.26	0.35	0.41	0.11	0.10	0.76	0.23	0.01	0.06	0.03	0.15	0.04	0.03	0.03	0.31	0.02	0.01
YC12	2.35	0.26	0.33	0.14	0.50	0.47	0.21	0.18	0.32	0.48	0.08	0.15	0.84	0.31	0.01	0.03	0.02	0.24	0.04	0.03	0.02	0.22	0.03	0.01
YC13	3.50	0.21	0.28	0.10	0.46	0.47	0.15	0.22	0.29	0.42	0.06	0.12	0.78	0.33	0.01	0.04	0.02	0.25	0.04	0.03	0.03	0.17	0.03	0.01
YC14	2.69	0.28	0.25	0.12	0.53	0.60	0.15	0.65	0.36	0.48	0.05	0.13	0.83	0.27	0.01	0.05	0.02	0.15	0.04	0.09	0.03	0.17	0.02	0.01
YC15	0.70	0.28	0.31	0.12	0.53	0.53	0.16	0.31	0.32	0.44	0.10	0.13	0.86	0.90	0.01	0.05	0.03	0.14	0.04	0.02	0.01	0.49	0.01	0.02
SJ2	2.56	0.43	0.29	0.26	1.28	1.02	3.97	2.65	0.22	1.69	0.13	0.51	1.43	0.28	0.04	0.03	0.05	0.10	0.03	0.02	0.04	0.26	0.01	0.01
SJ4	13.48	1.08	0.56	0.30	1.77	0.84	9.94	0.60	0.71	3.41	0.14	0.73	2.36	3.96	0.03	0.04	0.04	0.11	0.05	0.06	0.05	0.54	0.00	0.01
SJ6	2.84	0.67	0.35	0.22	1.21	1.07	2.29	3.80	0.38	1.56	0.20	0.46	1.62	3.68	0.03	0.04	0.05	0.22	0.05	0.05	0.03	0.36	0.00	0.01
SJ8	6.78	0.60	0.42	0.21	1.00	1.30	8.88	6.34	0.43	1.95	0.27	1.18	1.27	0.50	0.03	0.02	0.03	0.17	0.04	0.03	0.06	0.40	0.00	0.02
SJ10	0.64	0.40	0.48	0.17	0.86	0.88	0.27	0.28	0.49	1.03	0.07	0.28	1.54	1.53	0.01	0.06	0.05	0.62	0.04	0.09	0.06	0.45	0.05	0.04
SJ12	0.30	0.30	0.24	0.18	0.87	0.87	0.21	0.44	0.36	1.15	0.05	0.28	1.24	24.52	0.01	0.06	0.03	0.62	0.04	0.04	0.23	0.26	0.35	0.02
SJ14	0.38	0.25	0.13	0.33	1.38	0.80	0.15	2.47	0.18	1.49	0.07	0.42	1.56	0.85	0.03	0.01	0.01	0.44	0.02	0.02	0.04	0.33	0.01	0.01
SJ16	0.76	0.35	0.46	0.27	1.14	1.11	0.16	1.50	0.17	1.93	0.05	0.33	1.57	0.20	0.02	0.03	0.02	0.30	0.05	0.03	0.07	0.22	0.00	0.01
SJ19	0.95	0.38	0.26	0.21	1.46	1.06	0.23	2.11	0.23	1.63	0.21	0.49	1.75	0.34	0.04	0.03	0.02	0.16	0.04	0.03	0.03	0.25	0.00	0.00
SJ22	0.72	0.44	0.24	0.27	1.39	0.86	0.21	3.87	0.20	1.44	0.15	0.48	1.42	0.19	0.04	0.02	0.01	0.16	0.02	0.03	0.03	0.25	0.00	0.01

Table 15. Elements enriched with depth in C boreholes (Normalized by PAAS) [26]

Sample Name	Depth (m)	Enriched Element
C.2	18	Ti, Cr, U, Th, Mo, Pb, Zn
C.3	19	Ti, Cr, U, Th, Mo, Pb, Zn
C.4	20	Ti, P, Cr, U, Th, Mo, Pb, Zn
C.5	21	Ca, Ti, Cr, U, Th. Pb
C.7	23	Fe, Ca, Ti, P, Mn, Cr, U, Th, Mo, Pb, Zn
C.8	25	Fe, Ca, Ti, Mn, Cr, U, Th, Sr, Y, Mo, Pb, Zn
C.9	26	Ti, P, Cr, U, Th, Sr, Y, Mo, Pb,Zn
C.10	28	Ti, Cr, U, Th, Y, Mo, Pb, Zn
C.11	29	Ti, Cr, U, Th, Mo, Pb
C.12	30	Ti, Mn, Cr, U, Th, Mo, Pb, Zn
C.14	32	Ca, Ti, P, Cr, U, Th, Sr, Y, Pb
C.16	34	Ti, Cr, U, Th, Mo, Pb
C.17	35	Ca, Ti, Cr, U, Th, Sr, Mo, Pb
C.18	36	Ti, Cr, U, Th, Pb
C.19	37	Ti, Cr, U, Th, Pb
C.20	37,5	Fe, Q- Ti, Mn, Cr, U, Th, Mo, Pb
C.21	38	Ca, Ti, Cr, U, Th, Sr, Pb
C.22	39	Ti, Cr, U, Th. Mo, Pb
C.23	40	Ti, Cr, U, Th Pb
C.25	43	Ti, Cr, U, Th, Pb
C.27	45	Ti, Cr, U, Th, Sr, Mo, Pb
C.28	46	Ti, Cr, U, Th, Mo, Pb
C.29	47	Ti, P, U, Th, Y, Mo, Pb, Zn
C.31	50	Ti, U, Th, Mo, Pb, Zn
C.32	50	Ti, U, Th, Mo, Pb
C.33.a	52	Fe, Ti, U, Sr, Mo, Pb
C.33.b	53	Ti, Cr, U, Th, Mo Pb
C.34	56	Ti, Cr, U, Th, Mo Pb

Table 16. Elements enriched with depth in SJ boreholes (Normalized by PAAS) [26]

Sample Name	Depth (m)	Enriched Element
SJ.1	30	Si, Ca, Na, K, P, Cr, U, Th, Sr, Pb
SJ.2	36	Si, Ca, K, P, Mn, Cr, U, Th, Sr, Mo, Pb
SJ.3	40	Si, Fe, Mg, Ca, P, Mn, Cr, U, Th, Co, Ga, Hf, Sr, Pb, Zn
SJ.4	53	Si, Fe, Mg, Ca, K, P, Mn, Cr, U, Th, Hf, Sr, Zr, Y, Pb, Zn
SJ.5	54	Si, Ca, Na, K, P, Mn, Cr, U, Th, Co, Cs, Sr, Y, Pb
SJ.6	60	Si, Mg, Ca, Na, K, P, Cr, U, Th, Hf, Sr, Pb, Zn
SJ.7	67	Si, Mg, Ca, Na, P, Mn, Cr, U, Th, Hf, Sr, Y, Mo, Cu, Pb, Zn
SJ.8	68	Si, Fe, Mg, Ca, Na, K, P, Mn, Cr, U, Th, Sr, Y, Pb
SJ.9	80	Si, Fe, Cr, U, Th, Cs, Pb
SJ.10	81	Cr, U, Th, Cs, Sr, Mo, Pb, Zn
SJ.11	82	Ca, Mn, Cr, U, Th, Cs, Sr, Mo, Pb,
SJ.12	83	Cr, U, Th, Cs, Sr, Y, Mo, Pb, Zn
SJ.13	85	Cr, U, Th, Cs, Pb
SJ.14	86	Si, K, Cr, U, Th, Sr, Pb
SJ.15	88	Si, Na, K, P, Cr, U, Th, Sr, Mo, Pb
SJ.16	88,5	Cr, U, Th, Cs, Sr, Pb
SJ.17	90	Cr, U, Th, Cs, Sr, Pb
SJ.18	90,5	Cr, U, Th, Cs, Sr, Pb
SJ.19	91	K, P, Cr, Th, Cs, Sr, Pb
SJ.20	93	P, Cr, U, Th, Cs, Sr, Y, Pb
SJ.21	94	Si, Na, K, P, Cr, U, Th, Cs, Sr, Mo, Pb
SJ.22	95	Si, Na, K, P, Cr, Th, Cs, Sr, Mo, Pb
SJ.23	96	Na, P, Cr, Th, Cs, Sr, Pb
SJ.24	98	Si, Na, K, P, Cr, Th, Sr, Pb
SJ.25	100	Si, Cr, U, Th, Sr, Y, Pb

4.5. Geostatistics

The correlation matrices of the most important elements of all colors are shown in Table 17. According to this matrix, a proximity of 0.5 and above indicates a positive correlation. In this diagram, 0.51 with Fe-Mn, 0.63 with Mg-Mn, 0.54 with Fe-Na, 0.75 with Mg-Na, 0.97 with Mn-Na, and 0.69 with Si-Ti showed a high positive correlation of 0.58 with K-Ti. Again, the matrix shows that a proximity of -0.5 and below means a negative correlation. A negative correlation of -0.58 with Al-K, -0.65 with Fe-Ti, and -0.53 with P-Ti was shown. According to the major element dendrogram of all samples, these elements consist of 2 groups. The elements Ti, Si, K, and Al are in the first group. In the second group, the elements P, Fe, Na, Mn, Mg, and Ca are closely associated (Figure 15).

Table 17. Correlation matrix of major elements in all samples

	Si	Al	Ca	Fe	K	Mg	Mn	Na	P	Ti
Si	**1,000**	0,412	-0,207	-0,093	0,447	0,024	0,056	0,072	-0,294	**0,691**
Al		**1,000**	-0,349	0,263	**-0,582**	-0,282	-0,082	-0,101	-0,007	0,139
Ca			**1,000**	0,220	0,090	0,201	0,150	0,156	0,381	-0,294
Fe				**1,000**	-0,471	0,473	**0,513**	**0,549**	0,466	**-0,654**
K					**1,000**	0,204	0,011	0,046	-0,251	**0,582**
Mg						**1,000**	**0,631**	**0,750**	0,251	-0,352
Mn							**1,000**	**0,974**	0,385	-0,292
Na								**1,000**	0,441	-0,321
P									**1,000**	**-0,533**
Ti										**1,000**

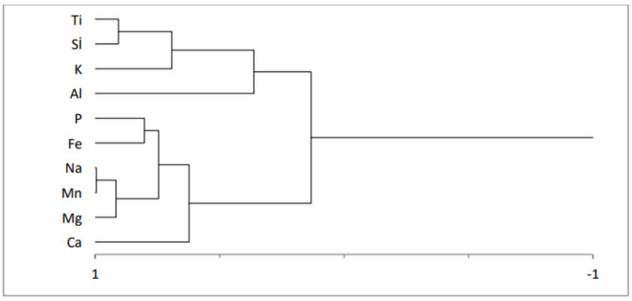

Figure 15. Dendrogram of major elements of all samples

The correlation matrices of trace elements for all samples are shown in Table 16. According to this matrix, it has a positive correlation of 0.80 with Rb-Cs, 0.64 with Rb-Th, 0.59 with Sc-Ni, 0.61 with As-Co, 0.59 with As-Cu, 0.57 with As-Mo, 0.53 with As-Ni, 0.64 with As-V, 0.79 with Be-Co, 0.95 with Be-Mo, 0.54 with Be-Pb, 0.85 with Be-Sb, 0.77 with Co-Mo, 0.58 with Co-Sb, 0.83 with Cu-Ni, 0.68 with Cu-V, 0.61 with Cu-Zn, 0.70 with Ge-Pb, 0.66 with Ge-V, 0.64 with Ge-Cd, 0.74 with Ge-U, 0.76 with Mo-Sb, 0.81 with Nb-Ta, 0.56 with Ni-V, 0.60 with Pb-Sb, 0.78 with Pb-V, 0.78 with Pb-Cd, 0.86 with U-Cd. It has a negative correlation of -0.51 with Rb-As, -0.53 with Rb-Co, and -0.52 with Sc-Ta (Table 18). According to the trace element dendrogram of all samples, we can group the elements into two main groups. While the elements Cs, Rb, Th, Ta, and Nb are found in the first group, the elements Ni, Cu, Sc, Zn, V, Cd, U, Pb, Ge, Mo, Be, Sb, Co, As, Sr, Hf, and Ga are found in the second group. These two groups are compatible with each other, while Zr and Bi are more distantly related (Figure 16).

Table 18. Correlation matrix of trace elements of all samples

	Rb	Sc	As	Be	Bi	Co	Cu	Ge	Mo	Nb	Ni	Pb	Sb	Ta	V	Zr	Hf	Zn	Sr	Cd	Cs	Th	U	Ga
Rb	1,000	-0,080	-0,514	-0,418	0,000	-0,537	-0,141	-0,221	-0,290	0,275	-0,289	-0,191	-0,422	0,156	-0,401	-0,213	-0,286	-0,410	-0,358	-0,312	0,805	0,646	-0,172	-0,137
Sc		1,000	0,049	-0,261	0,000	-0,175	0,447	0,351	-0,340	-0,458	0,596	-0,088	0,003	-0,527	0,266	-0,170	0,351	0,163	-0,124	0,030	-0,176	0,092	-0,093	0,025
As			1,000	0,597	0,000	0,615	0,597	0,365	0,574	-0,031	0,536	0,444	0,523	0,057	0,642	-0,224	0,444	0,417	0,337	0,429	-0,408	-0,281	0,411	0,359
Be				1,000	0,000	0,792	0,196	0,342	0,956	0,228	-0,039	0,542	0,858	0,394	0,475	-0,210	-0,099	0,328	0,455	0,384	-0,236	-0,326	0,538	0,266
Bi					1,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
Co						1,000	0,161	-0,043	0,779	-0,017	0,092	0,000	0,585	0,190	0,150	-0,240	0,035	0,081	0,461	-0,011	-0,383	-0,473	-0,010	0,061
Cu							1,000	0,371	0,211	-0,185	0,836	0,341	0,372	-0,134	0,689	-0,370	0,390	0,612	-0,125	0,440	-0,177	-0,054	0,325	0,305
Ge								1,000	0,206	-0,128	0,320	0,707	0,494	-0,105	0,669	0,039	0,193	0,495	0,246	0,644	-0,244	0,032	0,740	0,389
Mo									1,000	0,376	-0,071	0,463	0,765	0,482	0,425	-0,353	-0,123	0,301	0,374	0,258	-0,121	-0,253	0,444	0,394
Nb										1,000	-0,412	0,321	-0,038	0,818	0,116	-0,222	-0,104	-0,038	-0,153	-0,065	0,287	0,426	0,263	0,401
Ni											1,000	0,102	0,143	-0,383	0,563	-0,230	0,451	0,421	-0,232	0,247	-0,299	-0,130	0,066	0,139
Pb												1,000	0,609	0,334	0,788	0,044	0,069	0,575	0,132	0,788	-0,109	0,053	0,986	0,447
Sb													1,000	0,171	0,584	-0,205	-0,069	0,402	0,495	0,463	-0,233	-0,374	0,612	0,192
Ta														1,000	0,077	-0,234	-0,211	-0,027	0,096	0,048	0,241	0,283	0,302	0,215
V															1,000	-0,067	0,346	0,761	-0,049	0,675	-0,334	-0,188	0,752	0,544
Zr																1,000	0,182	-0,059	-0,028	0,153	-0,272	-0,283	0,076	-0,218
Hf																	1,000	0,298	0,095	0,227	-0,365	-0,059	0,068	0,213
Zn																		1,000	-0,061	0,767	-0,337	-0,218	0,577	0,504
Sr																			1,000	0,124	-0,276	-0,232	0,157	0,109
Cd																				1,000	-0,225	-0,102	0,816	0,280
Cs																					1,000	0,629	-0,117	-0,144
Th																						1,000	0,017	0,094
U																							1,000	0,382
Ga																								1,000

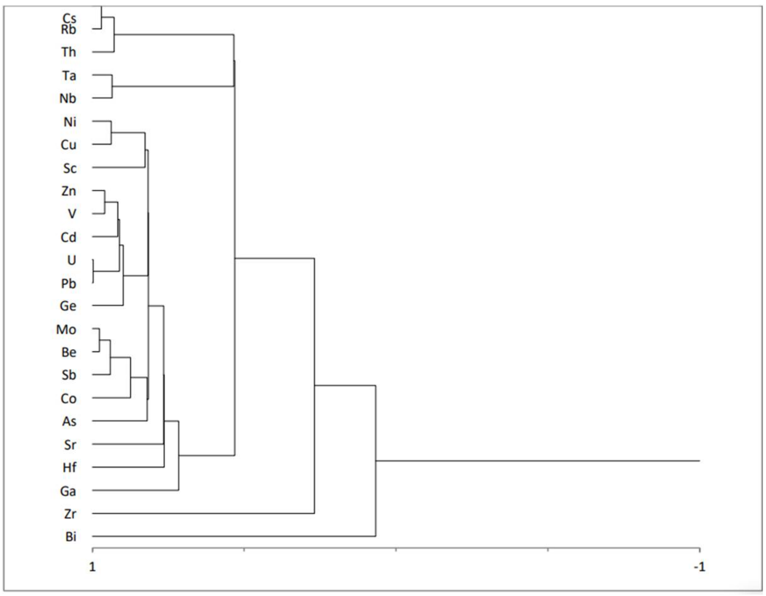

Figure 16. Trace element dendrogram of all samples

5. CONCLUSION

Rocks of organic origin are the result of physical and chemical changes and the accumulation of plant and animal remains in the water. These rocks, which generally form sedimentary rocks and have economic value, are composed of carbon, oxygen, hydrogen, nitrogen, sulfide, and various trace elements. For the organic content to be considered high, the carbon content must be greater than 70 percent by volume and 50 percent by mass. Although the inorganic elements in these rocks rich in organic matter have negative effects on the environment and human health, they can be important material resources that the technologies need when they are economically enriched [27,28].

Our results Show that the redox-sensitive, organophilic, carbonate mineral-forming and detrital elements of the oil shales in Sorgun Yeni Çeltek field are enriched according to the upper continental crust, post-Archean shale (PAAS), and average shale. The elemental enrichments of these organic-rich rocks were compared with organic-rich rocks or sapropels from different regions of the world, namely Peruvian coastal shelf sediments, Namibian mud lenses, Mediterranean sapropels (> 2 % TOC), Black Sea sapropels (B1), Cenoman/Turon (C/T) Demerara Uplift anoxic sediments, and C/T Gubbio anoxic sediments.

Silisium, which is enriched in almost all the samples studied, ranges from 1.03 to 1.38 times, P from 1.06 to 1.87 times, Cr from 8.02 to 18.49 times, U from 1.00 to 268.26 times, Th from 1.27 to 6.86 times, Sr from 1.1 to 5.24 times, and Pb from 1.12 to 4.54 times (Tables 15 and 16). Geostatistical evaluation of the studied samples showed a high positive correlation with Fe-Mn, Mg-Mn, Fe-Na, Mg-Na, Mn-Na, Si-Ti, and K-Ti for the main elements. It showed a negative correlation with Al-K and Fe-Ti and P-Ti. In the petrographic investigations carried out in the study area, detrital and authigenic origin minerals and enriched elements were found in the Çeltek Formation rock samples rich in organic material, depending on the depth. In addition to the main minerals pyrite, quartz, and kaolinite, smaller amounts of minerals such as illite, muscovite, plagioclase, gypsum, and dolomite were also detected. The geochemical analyzes of the samples suggest that the presence of the element Cu originates from clay minerals and quartz grains [29] and that it may be contributed by rocks such as granite and granodiorite, which form the basement rocks of the basin, as a possible source of U and Th in such deposits [4,5,30]. The presence and enrichment of elements such as Ge, Au, Pb, Zn, and U-Th indicate a hydrothermal effect [31]. In previous studies, the enrichment of Al, Si, K, and Cl in elemental enrichment in rocks rich in organic matter has been associated with terrestrial quartz grains, autogenous clay minerals, and chlorites [32]. Sulfur present in such rocks continues to exist in the environment, depending on its origin. Pyrite generally consists of syngenetic pyrite framboids, euhedral crystals, and massive grains in a reducing environment. Pyrite of framboidal origin was generally found in samples from the study area. It has been suggested that this type of pyrite is bacterial in origin [33]. However, Wiese and Fyfe [34] suggest that it is fungal in origin.

Quartz, the most abundant mineral in the samples, is one of the most important minerals of terrestrial origin. Among the clay minerals, it consists mainly of kaolinite and less of illite. The formations and origins of clays are generally authigenic [35]. These minerals are generally formed by the weathering of volcanic material [36,37]. Mica occurs as muscovite, and muscovite is generally detrital in origin. However, sometimes feldspar can be of authigenic origin and formed by superficial weathering processes [35]. The origin of gypsum may be epigenetic or exogenous [35]. Calcite is the most abundant carbonate mineral in rocks such as oil shale and coal, which are rich in organic matter. Since Ca-bearing minerals generally originate from seawater, they lead to the enrichment of elements such as P, K, Ca, Al, and Si [32]. Major elements such as Cr and Ti are generally enriched at all depths.

Trace elements such as U, Th, and Pb are also enriched at each depth, while Mo and Zn are enriched at some levels and consumed at some levels. The presence of trace elements in organic material may depend on many factors. While some of the trace elements are already present in the environment when the organic matter is formed, some of them are enriched or consumed depending on the maturation and decomposition processes they have undergone [38]. The most important factor affecting the abundance of these trace elements is mineral composition [39]. In addition to geological processes such as faulting, the mobility of elements in the environment due to climatic events can also lead to the enrichment of elements in minerals [40].

When examining the major and trace element correlations of the samples, the strong positive correlation between Rb and K is due to the presence of Rb in the potassium-forming minerals [41]. However, the presence of potassium feldspar and illite/muscovite in the samples could be the reason for the negative correlation between Rb and potassium in these samples [40]. In trace element analysis, the enrichment of elements such as Cu, Mo, Zn, Pb, V, and Cr is associated with clay minerals and organic material [42]. Pyrite minerals in organic material are also one of the most important factors affecting element enrichment [43,44].

Consequently, trace element contents in samples are affected by processes of change such as oxidation, evaporation, and maturation of organic matter. In mineral formation; temperature and the presence of oxygen; oxidation of mineral phase (oxidation of pyrite and marcasite to F2O3), dehydration of minerals (H2O and OH groups are released from clay minerals and mica), recrystallization of minerals (anisotropic transformation of SiO2, e.g. tridymite-cristobalite), formation of metastable phases, mineral formation at high temperatures (e.g., mullite), mineral crystallization from the melt (e.g., indivalite), and weathering processes (surface weathering) of some minerals can be effective. A combination of all these process factors can influence the element-mineral ratio in the study area.

According to these results, petroleum can be extracted from the oil shale of the Çeltek Formation. It is possible to economically extract naturally occurring radioactive elements such as U, Th, and K and other enriched trace elements such as Mn, Mg, Pb, Zr, Sr, K, Ti, Ca, Rb, U, and Co. However, this study should be supported by new scientific and economic project studies combining different disciplines (such as mining, chemistry, and metallurgy).

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AUTHOR'S CONTRIBUTIONS

The authors contributed equally.

CONFLICTS OF INTEREST

There is no conflict of interest.

RESEARCH AND PUBLICATION ETHICS

The author declares that this study complies with Research and Publication Ethics.

REFERENCES

[1] A. İ. Karayiğit, R. A. Gayer, E. Cicioğlu, and E. Eriş, "Mineralogy and Petrography of the Two Lower Eocene Lacustrine Coals, Sorgun and Suluova, Turkiye." Int. J. Coal Geol., vol. 34, no. 1–2, pp. 111–130, Oct. 1997, doi:10.1016/S0166-5162(97)00009-8.

[2] J. L Qian, J. Q. Wang, and S. Y. Li, "Oil Shale Development in China," Oil Shale., vol. 20, no. 3. pp. 356–359, 2003, ISSN 0208-189X, Estanian Academy Publishers.

[3] J. Hilger, "Combined Utilization of Oil Shale Energy and Oil Shale Minerals within the Production of Cement and Other Hydraulic Binders." Oil Shale, vol. 20, no. 3, pp. 347–355, 2003. ISSN 0208-189X, Estanian Academy Publishers.

[4] Z. D., Ekinci, "Mineral-Element Relationships in the Storage Environments of the Bituminous Shales of the Çeltek Formation (Sorgun-Yozgat)." MSc Dissertation, Yozgat Bozok University, Yozgat, Türkiye, 2017.

[5] B. Y. Pehlivanlı, "Organic Geochemistry and Rare Earth Element (REE) Characteristics of Oil-Bearing Shales of the Lower Eocene Çeltek Formation (Sorgun Yozgat Turkey)." Bozok University Project Coordination Application and Research Center, BAP project code, 2015 MMF/180, s.154. 2017.

[6] J. M. Hunt, Petroleum Geochemistry and Geology. W. H. Freeman and Company, pp. 617, 1979.

[7] B. Durand, J. Espitalie, G. Nicaise, and A. Combaz, "Étude De La Matière Organique Insgluble (Kérogène) Des Argiles Du Toarcien Du Bassin De Paris. L. Etude Par Les Procédés Optiques, Analyse Élémentaire, Étude En Microscopie Et Diffraction Électronique," Rev. Inst. Fr. Pet., vol. 27, pp. 865–884, 1972.

[8] D. M. Jarvie, "Total Organic Carbon (TOC) Analysis. Merrill, R.K., ed., Source and Migration Processes and Evaluation Techniques, Tulsa", Am. Assoc. Pet. Geol. Bull., pp. 113–118, 1991.

[9] B. Tissot and D. H. Welte, Petroleum Formation and Occurrence, 2. Edition. Springer-Verlag, Berlin, pp. 699, Feb. 1984.

[10] K. E. Peters and M. R. Cassa, “Applied Source Rock Geochemistry.” in The Petroleum System- from Source to Trap, L.B. Magoon and W.G. Dows eds., AAPG Memoir, vol. 60, pp. 93–117, 1994.

[11] E. T. Degens, Perspectives on Biogeochemistry. Springer, Berlin Heidelberg New York, pp. 423, May. 1989.

[12] R. D. Cody, “Adsorption and the Reliability of Trace Elements as Environmental Indicators for Shales.” J. Sediment. Petrol., vol. 41, pp. 461–471, June 1971, doi:10.1306/74D7229D-2B21-11D7-8648000102C1865D.

[13] H. J. Brumsack, “The Trace Metal Content of Recent Organic Carbon-Rich Sediments: Implications for Cretaceous Black Shale Formation.” Palaeogeogr. Palaeoclimatol. Palaeoecol., vol. 232, pp. 344–361, Mar. 2006, doi:10.1016/j.palaeo.2005.05.011.

[14] K. K. Turekian and K. H. Wedepohl “Distribution of the Elements in Some Major Units of the Earths Crust.” Bull. Geol. Soc. Amer., vol. 72, pp. 175–192, 1961, doi:10.1130/0016-7606(1961)72[175:DOTEIS]2.0.CO;2.

[15] P. Böning, H. J. Brumsack, M. E. Böttcher, B. Schnetger, C. Kriete, J. Kallmeyer, and S. L. Borchers, “Geochemistry of Peruvian Near-Surface Sediments.” Geochim. Cosmochim. Acta, vol. 68, pp. 4429–4451, Nov. 2004, doi:10.1016/j.gca.2004.04.027.

[16] S. L. Borchers, B. Schnetger, P. Böning, and H. J. Brumsack, “Geochemical Signatures of the Namibian Diatom Belt: Perennial Upwelling and Intermittent Anoxia.” Geochem. Geophys. Geosystems, vol. 6, no. 6, pp. 1–20, June 2005, doi:10.1029/2004GC000886.

[17] B. Warning and H. J. Brumsack, “Trace Metal Signatures of Mediterranean Sapropels.” Palaeogeogr. Palaeoclimatol. Palaeoecol., vol. 158, no. 3–4, pp. 293–309, May 2000, doi:10.1016/S0031-0182(00)00055-9.

[18] B. B. Jørgensen, M. E. Böttcher, H. Lüschen, L. N. Neretin, and I. Volkov, “Anaerobic Methane Oxidation and a Deep H_2S Sink Generate Isotopically Heavy Sulfides in Black Sea Sediments.” Geochim. Cosmochim. Acta, vol. 68, Issue 9, pp. 2095–2118, May 2004, doi:10.1016/j.gca.2003.07.017.

[19] S. E. Calvert and T. F. Pedersen, “Geochemistry of Recent Oxic and Anoxic Marine Sediments: Implications for the Geological Record.” Mar. Geol., vol. 113, pp. 67–88, July 1993, doi:10.1016/0025-3227(93)90150-T.

[20] H. J. Brumsack, “The Inorganic Geochemistry of Cretaceous Black Shales (DSDP Leg 41) in Comparison to Modern Upwelling Sediments from the Gulf of California.” in Summerhayes, C.P., Shackleton, N. J. (Eds.), North Atlantic Paleoocenography. Special Publication, Geological Society, London, vol. 21, pp. 447–462, 1986, doi: 10.1144/gsl.sp.1986.021.01.30.

[21] M. A., Arthur, H. J., Brumsack, H. C. Jenkyns, and S. O. Schlanger, “Stratigraphy, Geochemistry and Paleoceanography of Organic Carbon-Rich Cretaceous Sequences” in Cretaceous Resources, Events and Rhythms, eds.” Ginsburg, R. N. and Beaudoin, B. Kluwer Academic, pp. 75–119, 1990, doi: 10.1007/978-94-015-6861-6_6.

[22] J. R. Hatch and J. S. Leventhal, “Relationship Between Inferred Redox Potential of the Depositional Environment and Geochemistry of the Upper Pennsylvanian Missourian Stark Shale Member of the Dennis Limestone, Wabaunsee County,” Kansas, U.S.A. Chemical Geology, vol. 99, pp. 65–82, Sep. 1992, doi:10.1016/0009-2541(92)90031-Y.

[23] N. Kıratlı, and M. Ergin, “Partitioning of Heavy Metals in Surface Black Sea Sediments,” Appl. Geochem., vol. 11, pp.775–788, Nov. 1996, doi:10.1016/S0883-2927(96)00037-6.

[24] H. J. Brumsack, “Geochemistry of Recent TOC-Rich Sediments from the Gulf of California and the Black Sea.” Geologische Rundschau, vol. 78, pp. 851–882, Oct. 1989.

[25] S. R. Jacobson, “Petroleum Source Rocks and Organic Facies. Merrill, R.K., ed., Source and Migration Processes and Evaluation Techniques, Tulsa,” Am. Assoc. Pet. Geol. Bull., pp. 213, 1991.

[26] S. R. Taylor and S. M. McLennan, The Continental Crust: Its Composition and Evolution. Oxford: Blackwell Scientific Publication, pp. 312, 1985.

[27] J. J. Renton, “Mineral Matters in Coal,” in Mayers, R. A. (Ed.). Coal Structure. New York Academy Press. 1982.

[28] A. Kolker, R. B. Finkelman, C. A. Palmer, and H. E. Belkin, “Arsenic, Mercury and Other Trace Metals in Coal: Environmental and Health Implications” (Abstract, International Ash Utilization Symposium, Lexington, KY), 2001.

[29] R. Ivanov, “Native Metals (Gold, Silver, Copper) in Upper Cretaceus and Paleogene Sediments in the Western Fore-Balkan and the Central Balkan.” Geol. Miner. Resour., vol. 4–5, no. 19–23 (in Bulgarian with English abstract), 1999.

[30] Ş. Koç, A. Sarı and B. Yavuz Pehlivanli, “Variation of Trace and Radioactive Element in the Hatıldağ Oil Shale (HOS): Factors Controlling of Depositional Environment, Goynuk Area, Bolu, Turkiye.” J. Unconv. Oil Gas Resour., vol.15, pp. 84–97, Oct. 2016, doi:10.1016/j.juogr.2016.05.005.

[31] S. Dai, W. C. Zhang, R. Wardc, V. V. Seredin, J. C. Hower, X. Li, W. Song, X. Wang, H. Kang, L. Zheng, P. Wang, and D. Zhou, “Mineralogical and Geochemical Anomalies of Late Permian Coals from the Fusui Coalfield, Guangxi Province, Southern China: Influences of Terrigenous Materials and Hydrothermal Fluids”. Int. J. Coal Geol., vol. 105, pp 60–84, Jan. 2013, doi:10.1016/j.coal.2012.12.003.

[32] M. Yossifova, “Petrography, Mineralogy and Geochemistry of Balkan Coals and their Waste Products.” Int. J. Coal Geol. vol. 122, pp. 1–20, Feb. 2014, doi:10.1016/j.coal.2013.12.007.

[33] C. L. Chou, “Sulfur in Coals: A Review of Geochemistry and Origins.” Int. J. Coal Geol., vol. 100, pp. 1–13, Oct. 2012, doi:10.1016/j.coal.2012.05.009.

[34] R. Wiese and W. Fyfe, “Occurrences of Iron Sulfides in Ohio Coals.” Int. J. Coal Geol. vol. 6, pp. 251–276, Sept. 1986, doi:10.1016/0166-5162(86)90004-2.

[35] M. Yossifova, “Mineral and Inorganic Chemical Composition of the Pernik Coal, Bulgaria.” Int. J. Coal Geol., vol. 72, pp. 268–292, Nov. 2007, doi:10.1016/j.coal.2007.03.001.

[36] I. Kostova and A. Zdravkov, “Organic Petrology, Mineralogy and Depositional Environment of the Kipra Lignite Seam, Maritza-West Basin, Bulgaria.” Int. J. Coal Geol., vol. 71, pp. 527–554, Aug. 2007, doi:10.1016/j.coal.2006.06.006.

[37] W. Wang, Y. Qin, J. Liu J. Li and L. Yuan, “Mineral Microspherules in Chinese Coal and their Geological and Environmental Significance.” Int. J. Coal Geol., vol. 94, pp. 111– 122, May 2012, doi:10.1016/j.coal.2011.11.013.

[38] J. D. Saxby, “Minerals in Coal.” in Glikson, M., Mastalerz, M. (Eds.), Organic Matter and Mineralisation. Kluwer Academic Publishers, pp. 314–326, 2000, doi: 10.1007/978-94-015-9474-5_15.

[39] P. Zubovic, “Physicochemical Properties of Certain Minor Elements as Controlling Factors in their Distribution in Coal.” in Given, P. H. (Ed.), Coal Science. American Chemical Society, Advances in Chemistry, vol.55, pp. 221–231, Jan. 1966, doi: 10.1021/ba-1966-0055.ch013.

[40] J. Ciesielczuk, M. Misz-Kennan, J. C. Hower, and M. J. Fabiańska, “Mineralogy and Geochemistry of Coal Wastes from the Starzykowiec Coal-Waste Dump (Upper Silesia, Poland).” Int. J. of Coal Geol., vol. 127, pp. 42–55, Jul. 2014, doi:10.1016/j.coal.2014.02.007.

[41] C. R. Ward, D. A. Spears, C. A. Booth, I. Staton, and L.W. Gurba, “Mineral Matterand Trace Element Sincoals of the Gunnedah Basin, New South Wales, Australia.” Int. J. Coal Geol. vol.40, pp. 281–308, Jul. 1999, doi:10.1016/S0166-5162(99)00006-3.

[42] S. Dai, D. Ren, Y. Zhou, C. L. Chou, X. Wang, L. Zhao, and X. Zhu, “Mineralogy and Geochemistry of a Superhigh-Organic-Sulfur Coal, Yanshan Coalfield, Yunnan, China: Evidence for a Volcanic Ash Component and Influence by Submarine Exhalation.” Chem. Geol. vol. 255, pp. 182–194, Sept. 2008, doi:10.1016/j.chemgeo.2008.06.030.

[43] J. C. Hower, J. L. Campbell, W. J. Teesdale, Z. Nejedly, and J. D. Robertson, “Scanning Proton Microprobe Analysis of Mercury and Other Trace Elements in Fesufides from a Kentucky Coal.” Int. J. Coal Geol., vol. 75, pp. 88–92, Jul. 2008, doi: 10.1016/j.coal.2008.03.001.

[44] S. Dai, X. Wang, V. V. Seredin, J. C. Hower, C. R. Ward, J. M. K. O'Keefe, W. Huang, T. Li, X. Li, H. Liu, W. Xue, and L. Zhao, “Petrology, Mineralogy, and Geochemistry of the Ge-Rich Coal from the Wulantuga Ge Ore Deposit, Inner Mongolia, China: New Data and Genetic Implication.” Int. J. Coal Geol., vol. 90–91, pp. 72–99, Feb. 2012, doi:10.1016/j.coal.2011.10.012.